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NOTES ON THE TESTING OF ANTI-CORROSION PAINTS.*

By P. LABORDERE† and F. ANSTETT.‡

In view of the importance of protecting materials of construction from corrosion, by the application of paints, it would be of high interest to agree upon some method permitting to determine the quality of these products. Attempts have indeed been made to find some simple and rapid means of estimating the value of such paints by laboratory tests.

The chemical test, though indispensable for discovering possible adulterations, cannot be sufficient for this purpose; for in practice we have to compare paints of altogether different natures.

It is absolutely necessary to have recourse to mechanical tests.

Since the researches conducted up to the present have not given any really positive result, we have considered that it would be of interest to enter upon a fresh investigation of the subject.

At the two last congresses of the International Association for Testing Materials, reports have been presented on this question by Ebert (Brussels) in 1906, and by Camerman (Copenhagen) in 1905; both came to the conclusion that the results obtained were so uncertain that we could not for some time to come hope to discover the desired methods.

The researches previously undertaken by the American Society for Testing Materials have not led to any practical results either. The committee, consisting of manufacturers and consumers, nominated in 1902 by this society for the purpose of enquiring into the tests of materials capable of preventing the rusting of iron and steel, had some ingenious ideas which have been expounded in Report XVII of the Copenhagen Congress. The committee, however, appears to have interrupted its work without formulating any practical conclusion.

The question was thus fairly new. It was necessary to determine as well the constitution of the specimens as the nature of the tests to which they were to be submitted.

HOW TO PREPARE THE SPECIMENS.

The first difficulty experienced by all the enquirers consisted in the considerable influence which the support of the coat of paint exercises.

The substance which constitutes this support is necessarily rigid and strong, at least as much so as the skin of paint, and it plays therefore in these experiments a part which cannot be separated from that of the coating. How, then, under these circumstances are we to measure any quality of this latter: cohesion, elasticity, or permeability?

It was absolutely necessary, and the American Commission of 1902 foresaw this, to isolate the skin from its support.

The specimens to be tested should hence be films or pellicles of paint, detached from any support.

It was therefore only necessary to determine some method of preparation for these skins, such as to put them under conditions analogous to those of the practice, and to render them intercomparable.

It is practically impossible to obtain a coat of paint without any support. Our task was therefore to apply a coat of the paint to some provisional support and afterwards to get rid of the support.

Constitution of the Support.—We first thought of making use of a foil of tin which we intended to dissolve in mercury after having applied the paint.

This process, however, involves several inconveniences which would render the method of little practical value.

The tin must be applied in foil as thin as possible, so that it may rapidly be dissolved in mercury. We have, therefore, made use of sheets called "tin paper," having a thickness of 1/50 mm. But it is extremely difficult to stretch these sheets sufficiently to obtain a perfectly plane surface. There always remain between the sheet of tin and the board on which it is resting some air bubbles which can only be removed by a long and painstaking operation, and very often the foil will be torn in several places and the experiment be spoilt.

In order to dissolve the tin in mercury, moreover, we want a period of time that becomes longer and longer as the mercury becomes saturated with tin.

*Paper presented at the 6th Congress of the International Association for Testing Materials.

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Not to make the operation too tedious, therefore, the mercury has frequently to be renewed, which is a very laborious process, and even then we are not at all sure that the mercury may not exert some action upon the paint, when we are obliged to leave the two materials in contact for several hours.

We have thus, in order to meet the just mentioned difficulties, resolved to prepare some perfectly plane surface, and then to stretch on the surface some covering, soluble in water, to which we apply the paint. The separation of the coat of paint from its base can then easily be effected by simple immersion in water.

In order to obtain a perfectly plane surface, we simply had recourse to drawing paper, a sheet of this paper being stretched on a board in the ordinary way, after having moistened the paper.

As regards the covering, we have experimented simultaneously with solutions of gelatine and solutions of sugar.

The solution of gelatine might be used, but it labors under one grave difficulty: gelatine dissolves very slowly only in water, and it is therefore necessary, when taking off the skin, to keep the sheet covered with paint for at least 24 hours in water; this prolonged immersion is not without detrimental influence upon the paint.

The solution of sugar has, on the contrary, given us favorable results, and this is the procedure which we have finally adopted.

We therefore had prepared some perfectly plane board; in order to avoid all warping due to humidity, we took 3 sheets of oak and superimposed them with the fibres crossing at right angles. These sheets were glued and screwed together so as to obtain a very firm plane board.

On this board we stretch a sheet of drawing paper which has previously been moistened; we fix it to the four edges of the board by means of bars which fit in specially provided grooves. When we have assured ourselves that the sheet is well stretched after drying, we apply by means of a brush a solution of 25 per cent of sugar. To make sure that the covering is continuous, we repeat this operation a second time. We then allow to dry at an ordinary temperature.

Applying the Paint.—In order that the pellicles of paints, employed in different tests, should be comparable with one another, it is essential that they have a rigorously uniform thickness, at least in the moment of application; for the experimenter is not in a position to reduce the thickness during the course of the drying. It is indeed the thickness which characterizes the coat of paint; for we always attempt in practice to realize a practicably uniform thickness, whatever the density of the product employed may be.

We cannot rely upon the skill of the workman, who would turn out very different thicknesses, according to the density of the product; but we can realize the desired end by operating in the following manner:

We commence by determining the density very accurately under the conditions of the subsequent use of the paint; we can then immediately determine the weight of the coat of paint covering the surface of the support. For our tests we employ a film of 0.60 by 0.60 m. of a fixed thickness of 0.1 mm., which corresponds to the mean thickness of an ordinary coating.

We then weigh on a balance which is sensitive to the weight of 1 gr. the cup which contains the paint, as well as the brush; we apply the coat as uniformly as possible by reweighing from time to time the vessel and the brush, until the loss of weight corresponds to the weight of the coating we desire to apply. After several trials we easily succeed in this task.

In order to obtain a very uniform coating it is indispensable to make the strokes of the paint brush parallel to one another all over the surface of the sheet, and then to repeat this operation in a direction at right angles to the former. We repeat this three or four times, until the desired thickness has been secured. We have merely to take care to make the same number of strokes in the one direction as in the other.

The preliminary experiments demonstrated, however, that the skin of 1 10 mm. thus procured had too feeble a resistance to be convenient for experiments. We have therefore resolved to make the pellicles for the tests consist of two superimposed coatings, each of 1 10 mm., applied after a sufficient time interval (3 days) so that the first coating will be sufficiently dried at the moment when the second is being applied. We then allow the whole to dry. The drying should always take place under identical conditions. We have adopted a temperature of from 15 to 18°, in a dry atmosphere, protected from the direct rays of the sun.

Removal of the Pellicle.—The skin of paint should not be taken off before it is perfectly dry, as it might be torn, or at least more or less be deformed in a way which would spoil the experiment.

It is not easy, however, to determine the exact moment when the drying is sufficient.

We have not found any practical means of ascertaining in any precise manner the moment when the surface of the paint is perfectly dry. We are sure, however, to realize comparable conditions for all the tests by taking the skin off always at the end of six days. This period will be longer than the desiccation process of all good paints, even if we take the moment of applying the first coating of paint as the starting point, as we have done, because the surface exposed to the air dries more quickly than the interior particles of the skin.

At the end of the six days' period above indicated we cut the sheet of paper covered with the paint in strips having exactly a width of 0.05 m. and a length of 0.30 m., the cutting being effected in the sense of the last stroke of the brush. We afterwards cut each strip in two, so that we finally obtain 44 ribbons of 0.15 by 0.05 m.

Each of these ribbons is immersed in a vessel filled

with water at 15° C. After 10 minutes we take out the paper, and the skin of paint will come off without any difficuty. These skins are the test specimens. We stretch them out flat on blotting paper, the inner face above, in such a way as to complete the desiccation of the paint. We then wash this surface with a very soft sponge and water at 15° C., in order to remove any sugar solution which might still adhere to the paint.

We allow 24 hours to dry; the specimens are then ready for testing.

TESTS TO BE CONDUCTED.

The question arises now, what tests should be performed to enable us to classify the paints and to recognize—if only approximately—those which in practice give good results.

What we expect of a paint is that it should, under all circumstances, protect efficiently the substance which it covers. For this purpose it should be:

Tough and elastic, so that it will not split under the influence of strain and of any expansion of the support, nor under the action of blows. Impermeable so far as possible to all substances which might attack the support, particularly to water. Of considerable resisting power finally, so as to withstand as much as possible physical and chemical agents which might attack it (humidity, variations of temperature, acid vapours, particularly sulphurous anhydride produced by the combustion of certain coals, and sulphuretted hydrogen).

The tests should bring out these different qualities.

Tenacity.—As a measure for the tenacity, we have taken the tensile strength of the pellicle prepared in the way indicated.

This strength can easily be measured.

The apparatus employed for this purpose comprises merely two jaws which grip the extremities of the skin. One of these we suspend from a fixed hook, while the other supports a receptacle into which we pour fine shot until the skin is broken. When we weigh the receptacle, as well as the lower jaw, we find the total load of rupture. For skins about 2/10 mm. in thickness, the loads of rupture are sufficiently high clearly to differentiate between the cohesions of the different paints, or rather the cohesions of different skins of the same paint submitted to different treatments.

For example, a skin of ripolin (a lacquer composed of zinc white, linseed oil, some essence and resinous gums) has given us a strength of 5.115 kg. with a width of 0.05 m.

We possess, therefore, a method enabling us to study the paint itself and to measure its cohesion with precision.

A technical difficulty arises, however, because we must find some jaws which will firmly grip the skin without tearing it.

We have secured this object by making each jaw consist of a small cylinder of aluminum, of 0.01 m. diameter, split into two equal bodies by a diametrical plane. The extremity of the skin is placed between these two half-cylinders, which are pressed against one another by means of two slightly truncated conical screws fixed to the two extremities of the cylinder in parts prepared for the purpose. The skin is then once rolled round the whole cylinder, and the cylinder is suspended by its two ends in a stirrup arranged in such a fashion that it cannot turn.

The useful length of this specimen, reckoned between the generatrices of the two cylinders along which the contact is effected, is always taken equal to 7 cm.

For certain paints which are altogether devoid of elasticity and which cannot be rolled, we content ourselves with gripping the skins betwen the jaws and with maintaining the useful length between these.

The two stirrups are themselves hooked either to the fixed support or to the receptable for the shots by curved parts which permit them to place themselves parallelly, so that the tension stress shall be the same at all parts of the skin.

Thanks to this device, we have been able always to obtain a rupture of the skin near its middle and under the effect of very nearly the same loads with different pellicles of the same product.

Elasticity.—We have thought of measuring the extension of the skin before its rupture by progressive loads in the previous experiment. For that purpose, however, a delicate apparatus would have been required.

We therefore preferred to make use of a folding test. A specimen folded upon itself is placed between two hard and plane horizontal plates, for instance, two pieces of glass, the lower one resting on a table and the upper one being gradually charged with weights. We note the charge under which the skin breaks at the fold.

Permeability.—We have to place on the specimen a tube of a given height, e. g., 10 cm., kept full of water, and to measure the quantity of water which traverses the skin in a certain time.

For these two tests we make use, not of special specimens, but of the fragments of the specimens which were broken in the traction tests.

Experience has proved that these fragments present, so far as we are concerned, the same qualities as new specimens.

We have also convinced ourselves that we might have repeated the tension tests with the ruptured fragments of the specimens without modifying the results. We have, however, preferred to avoid all criticism, and for this reason we have made all the rupture experiments with specimens of constant length.

Resistance to the action of physical and chemical agents.—It is impossible to investigate all the agents under this heading which might be met with in reality.

We have selected those which appear to us the most important and the most characteristic: humidity, heat, and sulphurous anhydride.

To measure the alteration of the paint by these

agents we have submitted specimens, prepared in a similar way, to the tests for tenacity, elasticity and permeability, as described above, before and after the action of these forces.

Destructive actions have been realized under the following conditions:

Humidity: In order to exaggerate the effects of prolonged moisture and to be able rapidly to arrive at some results of practical value, we have completely immersed the test skins in water at 15°. This immersion has been obtained by suspending the skins in a beaker filled with water, all folding being avoided.

Heat: Four pellicles have been suspended in a hot air oven kept day and night at a temperature of 50°.

TABLE I.—FIRST SERIES: RIPOLETTE: RESULTS OF THE TENSION TESTS.
(Total load for breaking the specimen 0.05 m in width.)

Age of the specimens at the time of the tests.	Specimens kept in air at a temperature of from 15 to 18°	Specimens exposed to moisture.	Specimens kept in hot air at 50°.	Specimens exposed to sulphurous anhydride.
7 days.....	0.672 kg. 0.651 kg. 0.644 kg.	Pellicles kept for 14 days in the atmosphere, then immersed in water at 15° for 14 days.	Pellicles kept for 14 days in the air, then for 14 days in hot air at 50°.	Pellicles kept for 14 days in the air, then exposed to SO_2 for 2 days.
16 days.....				Breaking load: 0.179 kg. 0.339 kg.
28 days.....	0.945 kg. 0.882 kg. 1.070 kg. 0.885 kg. 1.242 kg.	0.392 kg.[1] 0.410 kg.	1.370 kg. 1.435 kg. 1.247 kg. 1.392 kg.	On the fourth day of the exposure to SO_2 the ribbons broke under their own weight. Width 63 mm.: increase: 26%.
39 days.....				Kept 37 days in the air, then exposed for 2 days to SO_2. 0.570 kg. 0.467 kg. 0.695 kg. 0.645 kg.
60 days.....	1.390 kg. 1.325 kg.			On the third day the ribbons which had remained in SO_2 broke under their own weight.

[1] At the moment of the test the specimen had a width of 62 mm. that is an increase of 24%.

TABLE II.—SECOND SERIES: MINIUM (RED LEAD): RESULTS OF TENSION TESTS.

Age of specimens at the time of testing.	Specimens kept in air at temperatures from 15 to 18°.	Specimens exposed to moisture.	Specimens kept in hot air at 50°.	Specimens exposed to sulphurous anhydride.
8 days.....	0.748 kg. 1.300 kg. 1.455 kg. 1.255 kg.	Pellicles kept 14 days in air, then immersed in water for 15 days.	Pellicles kept 14 days in air, then 15 days in hot air at 50°.	Pellicles kept 14 days in air, then exposed to SO_2: after one day's exposure the pellicle breaks up and falls under its own weight.
29 days.....	1.310 kg. 0.630 kg. 1.950 kg.	The width has increased by 16%. The pellicle has become very brittle and breaks under a load of a few grammes.	0.600 kg. The pellicles have turned very brittle, only one strength test could be made.	One pellicle left 14 days in air and then 2 days in SO_2 breaks under the following loads: 0.629 kg. 0.483 kg. 0.895 kg.
31 days.....		Pellicle kept 11 days in air, then immersed in water for 15 days, afterwards put into the oven at 50° for 2 days. 1.252 kg. 2.260 kg.		
40 days.....		Pellicles kept 14 days in air, then 15 days in water, then 11 days in air. 0.737 kg. 1.062 kg.		
51 days.....		Pellicles kept 14 days in air, then 15 days in water, then 22 days in air. 1.010 kg. 0.740 kg.		

Sulphurous Anhydride: Four pellicles have been suspended in a beaker through which a current of sulphur dioxide was being passed.

The tests, which we have conducted up to the present and of which we give details lower down, have had the main object of settling the normal conditions to be adopted for comparative testing. We had not made breaking tests at those dates.

UTILIZATION OF THE SPECIMENS.

We would recommend the following procedure:

Of each paint 44 specimens are prepared, of 0.15 by 0.05 m., and utilized as follows: 12 specimens serve as standards; they are kept in dry air at a temperature of from 15 to 18°, and tested for tension:

Four of these, at an age of 14 days—that is, 8 days after pulling of the pellicle, as explained above; 4 at an age of 21 days; 4 finally at an age of 28 days.

These periods appear of sufficient length, in the light of our experience, to bring out the differences between various paints, and it is desirable, in the interest of the acceptance tests, to shorten the tests.

Eight specimens are kept for 14 days in the air, counting from the application of the first coat of paint, then immersed in water and submitted to the tensile tests, 4 after 7 days and the others after having been kept for 14 days in water—that is to say, at an age of 21 and 28 days.

Eight specimens are kept for 14 days in the air, then put into the oven at 50°, and submitted to tensile tests after having been 7 and 14 days in the oven, i. e., at an age of 21 and 28 days.

Eight specimens are kept for 14 days in the air, then exposed to vapors of sulphurous anhydride and submitted to the breaking test, if their condition permits of making the test, after having been exposed to the SO_2 for 7 and 14 days, i. e., they are broken at an age of 21 and 28 days.

There remain:

Eight specimens for recommencing certain tests in cases of accidents.

Total: 44 specimens.

The starting point of the age of the specimens must precisely be decided upon; it might be the moment of the first application of the paint, in analogy to the practice of cement testing.

The means are in each instance the means of 3 tests, the lowest value, which will often be abnormal, having been eliminated in each case.

The fragments of specimens which have been submitted to the tension test serve for the determination of the elasticity (by folding) and of the impermeability, on the same day on which the tension test was made.

TABLE III.—THIRD SERIES: RIPOLIN: RESULTS OF TENSION TESTS.

Age of the specimens at the time of testing.	Specimens kept in air at temperatures from 15 to 18°.	Specimens exposed to moisture.	Specimens kept in hot air at 50°.	Specimens exposed to sulphurous anhydride.
11 days.....	2.100 kg. 2.600 kg. 2.520 kg.			
		Pellicles kept for 12 days in air, then immersed in water at 15° for 2 days.	Pellicles kept 12 days in air, then 2 days in hot air at 50°.	Pellicles kept 12 days in air, then 2 days in SO_2; the width has increased by 20%.
14 days.....	2.860 kg. 2.900 kg.	0.860 kg. 1.860 kg.	2.190 kg. 4.750 kg. 4.700 kg.	0.590 kg. 0.950 kg.
		Pellicles kept for 12 days in air, then immersed in water for 9 days.	Pellicles kept in air for 12 days, then 2 days at 50°.	The other pellicles left in SO_2 have broken on the third day under their own weights.
21 days.....	3.105 kg. 1.865 kg. 3.310 kg.	0.465 kg.	5.095 kg. 5.115 kg.	
		The pellicle has increased in width by 21% and has become very inconsistent; only one rupture test succeeded.		

Tables I, II and III show the respective results of tension tests on the following: 1st series: Ripolette: density, 1.610; thickness of layer, 0.12 mm. 2nd series: Minimum (Red Lead); density, 2.880; total thickness of two layers, 0.02 mm. 3rd series: Ripolin; density, 1.600; total thickness of two layers, 0.215 mm. In these first experiments the layer of paint was spread without measuring the applied quantity, the object being first to study the applicability of the mode of preparing the specimens.

RESULTS.

The experiments of practical utility are not numerous so far. They concern three paints: Ripolette, consisting of a mixture of linseed oil, essence of terebenthine, resins and zinc white; minium (red lead) stirred into a mixture of oil and essence; ripolin, of a composition analogous to that of ripolette.

We cannot yet draw very definite conclusions, all the less because these researches were, as stated above, undertaken for the purpose of studying methods, and were not conducted under rigorously comparable conditions, therefore.

We state the results, however, at least in so far as the tension tests are concerned, the technics of which have well been settled.

As regards the elasticity and permeability, we prefer to postpone publication until we shall have improved the mode of operation.

It is from these experiments that we concluded that it would be sufficient to make the tests at an age of 21 or 28 days. The degradation of the pellicles kept in water and in sulphur dioxide is much advanced by this time. We notice also how much keeping in hot air hastens the desiccation of the paint and accelerates the hardening which corresponds to its ageing.

The differences shown by the different products are sufficient for the purpose of easy classification.

Five or more factories for the production of fuel from petroleum, benzine, and residual oils, in combination with peat or vegetable pulp, are to be constructed in Mexico. The contractor will invest not less than $100,000 in gold in the equipment of these factories, which will be completed within three years after the approval of the plans.

The Indiana Steel Co. of Gary, Ind., has been conducting some experiments with the use of tar as a fuel for its open-hearth furnaces in place of producer gas. The result of these operations is stated to have been very successful, and at the present time two furnaces in open-hearth unit No. 1 are being operated exclusively with tar. The tar is used in its liquid state as it comes from the by-product coke oven plant and is handled very much like fuel oil. The burners are similar to those used for oil and the tar is atomized with steam.

According to the customary statistics annually published by the firm of Hecht, the total production of wild and plantation rubber throughout the world in the 12 months ended with June 30, 1912, amounted to 93,669 tons, as compared with 79,302 tons in the previous year and 76,026 tons in 1909-10. On the other hand, the total consumption in 1911-12 is returned at 99,564 tons, as contrasted with 74,082 tons in 1910-11, or an increase of 25,482 tons, whereas the quantity consumed in 1909-10 was only 4,037 tons in excess of the preceding year. The world's stocks of rubber on July 1, 1912, are reported to have been 10,181 tons, as against 12,563 tons on the same date in 1911. This is a reduction of 2,382 tons, and compares with an increase of 5,565 tons on July 1, 1911, as contrasted with the position on July 1, 1910.

PAINTS FOR METALLIC STRUCTURES.*

The necessity for protecting all metals, and particularly structural iron and steel, from corrosion, by the application of suitable paint coatings, has long been recognized as a subject of great importance. The tendency to corrode and rust is characteristic of the element iron, and follows it to a greater or less degree through all of its alloys and combinations. While it is probably true that a homogeneous and carefully made metal undergoes the rusting processes more slowly and in a different manner from badly segregated and hastily made material, nevertheless, it must be conceded that wherever iron or steel is put into service protective coatings are essential to their proper maintenace, except in such cases as may be instanced in the interior of boilers, where such coatings cannot be practically maintained. For the protection, however, of structures of all kinds, such as bridges, railroad equipment and the numerous forms into which iron is fabricated, there should be used the best materials obtainable, in view of the fact that the thickness of the protective films that are called upon to withstand the effects of severe exposure, seldom exceeds a very small fraction of a millimeter. The efficiency of a paint for metallic structures depends upon (1) the excellence of the vehicle used, (2) the influence of the pigment on the vehicle with which it is mingled, and (3) the influence of the pigment upon the underlying metal. This last phase of the subject, namely, the possible influence of the pigment upon the underlying metal, is the feature of our subject which has received the greatest amount of attention from investigators since the last meeting of the Congress.

There is a vast amount of literature on the subject of protective coatings, which it would be quite impossible to review in a report of this nature. For many years past a number of authorities have investigated and published reports on protective coatings for metallic structures, but up to the period embraced in the last three years the principal object in experimental tests was to determine the combination of vehicle and pigment, which promised at the same time the greatest excluding value for water and gases of the atmosphere which would induce corrosion, and the greatest longevity of the paint films.

During the last few years a number of independent investigators have attacked the general subject of the corrosion and atmospheric rusting of iron and steel, with the result that the electrolytic explanation of the mechanism of the corrosion reactions has been advanced and successfully defended. Space will not permit in this report of the discussion of the underlying facts upon which the electrolytic theory of corrosion is based,[1] but it is sufficient to state that by far the greater number of authorities who have published

*Official report of Allerton S. Cushman, Washington, D. C., presented at the Sixth Congress of the International Association for Testing Materials.

upon this subject within the last three years have become convinced that the electrolytic explanation, based upon the modern theory of solutions, can be made to account for the mechanism of all rusting and corrosion reactions.

As soon as the electrolytic theory appeared, it was a natural corollary from this working hypothesis to assume that the pigment particle of a protecting coating might readily have some effect either in stimulating or inhibiting the corrosion reactions which were tending to take place upon the surface of the underlying metal. The first suggestion in regard to this possibility was made by the writer, before the American Society for Testing Materials, at the annual meeting in 1907.[2] The following year, this matter was carried still further and discussed more in detail in another paper.[3] The fact that chromic acid and its soluble salts had been discovered by a number of observers to render the surface of iron passive, and thereby to check or inhibit corrosion, seemed to promise a new field of investigation, in the production of protective coatings. At the same time, the well known prohibition of rusting afforded by strong alkaline solutions appeared also to indicate that the well known protective power of many basic pigments might be explained from the same point of view. Many highly basic pigments have been found excellent for prime coatings, as is instanced in the well known and almost universal use of red lead for this purpose. At the same time, a great difference of opinion has existed among engineers in regard to the value of red lead, so that it could not be said at any time that the problem of protecting iron and steel had been solved beyond the possibility of great improvement. One of the points brought out in the earlier researches of your reporter was that the protective effect of a given paint might be entirely overcome by the presence of stimulating or accelerating impurities. It has several times been pointed out that in cases in which in a protective coating inhibitive pigments are contaminated with stimulating impurities, the two actions would be matched off against one another, with the effect that the attack upon the underlying metal would take place vigorously at weak points where the protective action could not be efficiently maintained.[4] In fact, it appears to be the case that whenever we have the two opposite actions going on at the same time, the attack is localized and even rendered more severe at given places than in other cases in which no such counter-action is possible. To those who have not followed the published results of investigations along these lines within the last three years, it should be stated that by stimulative action of a pigment in a so-called protective coating is meant either chemical or electrolytic action, which induces the rapid corrosion of the metal with which it may find itself in contact. On the other hand, by inhibitive action or inhibition is meant the counteraction which tends to check or retard the reactions which lead to corrosion. If it were possible to devise a paint vehicle which would harden under the influence of oxygen of the atmosphere into a perfect exclusive film into which or through which water could not penetrate, the effect of the pigment mingled with the vehicle would be of little or no importance in any consideration of our subject. It is a well known fact, however, that no paint film or vehicle as yet discovered or devised has shown perfect excluding power. It may be admitted that the addition of certain high class gums and other varnish materials will greatly increase the excluding power of the vehicle, and also lengthen its life. It must, however, be admitted that the action of moisture and the vapors and gases of the atmosphere will gradually attack and change the nature of even the most expensive and high grade coatings, while at the same time it must be remembered that the annual and diurnal contractions and expansions of metal are continually tending to disrupt and destroy protective coatings, owing to unequal and changing coefficients of expansion. In the light, therefore, of the most modern investigations, it would appear that after everything which is practical and economically possible has been done to improve the paint vehicle, the nature of the pigment must be given the most careful consideration, as the acceleration or retardation of the rusting processes must depend to a large degree upon the effect of the pigment on the underlying surface.

Following the suggestion that the various types of substances used as pigments in protective coatings might exert a stimulative or an inhibitive action on the rate or tendency of corrosion of the underlying metal, it was further suggested on theoretical grounds that slightly soluble chromates should exert a protective action when employed as pigments, by maintaining the surface of the iron in a passive condition in case water and oxygen penetrated the paint film.[5] Also, in view of the well known fact that alkalies inhibit, while acids stimulate, the corrosion of iron, it was recommended that the action of more or less pure pigments on iron in the presence of water should be thoroughly investigated. This recommendation was made by Mr. G. W. Thompson, who suggested also the method of investigation. Three years ago Committee U (now Committee A-5) of the American Society for Testing Materials invited the co-operation of Committee D-1 (then known as Committee E) in carrying out this investigation, and a special sub-committee representing the two main committees was appointed. The method and results of the water pigment tests[6] have previously been reported and published, and need not be given in detail at this time. Briefly described, the method consisted of immersing samples of steel in water suspension of

[1] Whitney, Jour. Am. Chem. Soc., XXV, 1, 394 (1903). Cushman. Proc. Am. Soc. Testing Materials, VII, 211 (1907). Walker, Jour. Am. Chem. Soc., XXIX, 1251, XXX, 473 (1907). Heyn and Bauer, Jour. Iron and Steel Inst., 78, 663 (1908).

[2] The Corrosion of Iron. Allerton S. Cushman. Proc. Amer. Soc. for Testing Materials, Vol. VII., p. 211 (1907).

[3] The Inhibitive Power of Certain Pigments on the Corrosion of Iron and Steel. Allerton S. Cushman. Proc. Amer. Soc. for Testing Materials, Vol. VIII, 605 (1908).

[4] Cushman, los. cit., see also Friend, Iron and Steel Inst. Carnegie Scholarship Memoirs, III, 1 (1911).

[5] A. S. Cushman. Bull. 30, Office of Public Roads, U. S. Dep't Agr. (May 10, 1907).

the various pigments and blowing air through the containers for definite periods of time, the corrosion being measured by the loss in weight sustained by the test pieces after being carefully cleaned and dried. About fifty pigments which are in more or less common use for painting steel were purchased in the open market and distributed among the various members of the committee, who agreed to carry out the work. Each investigator worked independently of the others, except that the same general method was followed; the time of exposure to the corroding action, however, varied in the work of the different experimenters. When the results were compared and analyzed by the sub-committee, it was felt that the general agreement obtained by the several investigators was striking and indicated that the subject should be followed up by a series of service tests in connection with the usual oil vehicle. As a result of the water tests, the sub-committee tentatively divided the pigments into "inhibitors," "stimulators" and "indeterminates." The word "indeterminate" was selected after considerable discussion, because the words "neutral" and "inert" already possessed a special meaning, as applying to paint technology. The committee took occasion to emphatically point out that in adopting this tentative classification, the words "inhibitive" and "stimulative," as used by them up to the time of their report, applied only to the results obtained in the water tests, and the inference that the results decided which class the pigment should fall in when made into a paint with the usual vehicles was not justified. In order to emphasize this point, it was agreed by the committee to qualify the classification so as to speak of the various materials tested as "water stimulative" or "water inhibitive." As was to be expected as a result of these tests, some difference of opinion developed in regard to whether or not the water tests would be found to have anything to do with the value of the pigments when properly mingled with an oil vehicle and laid out on a surface of steel in the form of protective coatings.

A simple method of determining the water inhibitive nature of a pigment without the necessity for laboratory facilities has been recently published.[7] In order to follow this question up, the Paint Manufacturers' Association of the U. S. made an appropriation for the installation at Atlantic City of a number of steel panels which would be painted under test conditions with the pigments which had been investigated in the water tests. These Atlantic City test panels, which will be described more fully later on, were not erected, as has sometimes been supposed, in order to determine the best protective coating in the form of a paint, which could be evolved for the protection of steel under service conditions, but merely for the purpose of determining by test whether the theory which has come to be known as the inhibition theory of paint protection was justified by the facts obtained in a systematic series of exposure tests lasting over a considerable period of years.

[6] Proc. Amer. Soc. for Testing Materials, IX, 203 (1909).

It may here be pointed out that the value of some of the pigments which have now come to be termed "inhibitors" was in many cases fully realized a number of years ago, and several of these pigments have been in very general use for the protection of metal, although no explanation was attempted of the underlying reasons for the protection which they clearly afforded to the underlying surface. As far back as 1900 Andes[8] claimed to have obtained excellent results from the use of potassium chromate as a material for preventing the corrosion of iron and steel. Andes gave no reason, however, for the apparent immunity from rust, which resulted when steel plates were coated with aqueous solutions of the chromate salts. A number of years ago Wood[9] pointed out that good results had been obtained by the application of chromate pigments, but this author had no explanation to offer for the underlying causes of the protective action. Wood also pointed out the protective value of such basic materials represented by the sublimed leads, red lead, litharge, etc. The alkaline chromates and bichromates, as is well known, are very soluble in water and cannot be properly ground into an oil vehicle in order to form paints. It is, however, well known that the alkaline earth chromates, as well as some of the metallic chromates which are only very slightly soluble in water, are easily ground with oil to form paste paints which possess excellent spreading and covering values. In fact, the chromate pigments have long been recognized as possessing all of the requisites for making good paints. Many of the chromate pigments, however, are manufactured by precipitation under acid conditions, and though protective in their own nature, are liable to contain by inclusion rust stimulating impurities.

As a result of the inhibitive water tests which have been described above, nearly all the pigments of a strongly basic nature proved to be active inhibitors of corrosion. One pigment which combines a basic value together with the protective effect of a slightly soluble chromate is American Vermilion, a basic chromate of lead which, as will be seen later on, has led all the pigments tried on the Atlantic City test panels. In this connection, it is interesting to record that previous to the theoretical considerations here described, Mr. W. G. Scott, of Chicago, a prominent paint technologist, has described the excellent results which he had obtained by the use of this pigment in the painting of a number of iron shutters upon a large storehouse building. Scott had not selected this material on account of any known protective value that it had, but has recorded the fact that after ten years' service the paint was still giving excellent results, having served to protect the metal over which it was placed in a very efficient manner.[10]

In addition to the good results which have been reported from the use of properly selected chromate pigments, there are many references in the literature to

[7] Corrosion and Preservation of Iron and Steel (Cushman-Gardner), McGraw-Hill Book Co. (1910), p. 243.
[8] L. E. Andes. Iron Corrosion (1900).
[9] M. P. Wood. Rustless Coatings. Wiley & Sons (1905).

the good effects obtained by the use of properly selected basic pigments which hydrolize with a slightly alkaline reaction. As an instance of these, we may refer to the good results obtained by some of the basic slag pigments, as well as the generally well known protective effect of the oxides of lead and zinc. Basic carbonate-white lead (corroded white lead) and basic sulphate-white lead (sublimed white lead) are also in the same class. Portland cement has frequently been suggested as a pigmentary substance, undoubtedly owing to the well known alkaline effect which is obtained by the hydrolysis of this substance. It may be pointed out here, however, that if the alkaline reaction of a pigment is strong, the effect upon the oil vehicle will be too great and will rapidly saponify it, thus defeating the object of the use of the pigment, by a rapid destruction of the vehicle. It is probable that good results can be obtained by taking advantage of highly basic pigments for prime coating material, provided the top coatings are specially designed to provide the maximum exclusion of moisture and the atmosphere. In fact, this procedure has been recommended by several paint technologists.

Recently, the value of the inhibitive theory as it applies to paint protection of metals, has been recognized in Europe, notably by Friend,[11] who, in spite of the fact that he combats the electrolytic theory of corrosion and returns to the old acid theory, nevertheless recommends the employment of the more insoluble chromates and basic chromates, such as those of lead and zinc as pigments in paints to be applied to the surface of iron as a protection against undue corrosion. Dr. Friend also agrees with the writer in pointing out that the pigments should be free from soluble impurities, such as stimulate corrosion, for otherwise the selection of such pigments may do more harm than good. All the authorities who have accepted the more recent theories of corrosion, recognize that the use of

TABLE NO. 1.—SECOND INSPECTION OF STEEL PAINT TEST PANELS AT ATLANTIC CITY, N. J.

Panel No.	Pigment.	W. H. Walker.	P. H. Walker.	H. A. Gardner, Chairman.	C. Chapman.	Average.
1	Dutch process white lead	2	3	3	5	3.7
2	Quick process white lead	4	4	3	6	4.2
3	Zinc oxide (XX)	1	1½	1	2½	1.5
4	Sublimed white lead	9	9½	9	8½	9.0
5	Sublimed blue lead	9	9½	9½	7½	8.8
6	Lithopone	2	1½	2	3½	2.2
7	Zinc lead white	3	4	5	7	4.7
9	Orange mineral	9	9	9	6½	8.3
10	Red lead	9	9	9	6½	8.3
12	Bright red oxide	8½	9	8	7	8.1
14	Venetian red	7	9	7	9	8.0
15	Princess metallic brown	5	7½	6	8	6.3
16	Natural graphite	6	9	4	9½	6.8
17	Artificial graphite	5	7½	4	7	5.9
19	Lamp black	5	7½	5	8	6.3
20	Willow charcoal	9	8½	9	9	8.8
21	Carbon black	7	8½	5	8½	7.2
24	Yellow ochre (French)	5	7	2	8	5.5
27	Rarytes (natural)	1	1	1	—	0.7
28	Rarytes (precipitated)	2	1½	2	2	1.8
29	Calcium carbonate (whiting)	—	—	—	—	—
30	Calcium carbonate (precipitated)	—	—	—	—	—
31	Calcium sulphate (gypsum)	1	1	1	3	1.7
32	China clay (caolin)	6	6	7	6½	6.3
33	Asbestine (magnes. silicate)	5	4½	6	5	5.1
34	American vermillion	10	10	10	10	10.0
36	Lead chromate	7	7½	8½	8	7.7
39	Zinc chromate	9	9	10	9½	9.5
40	Zinc and barium chromate	9	9½	10	9½	9.5
41	Chrome green (blue tone)	10	10	10	9½	9.8
44	Prussian blue W. S.	9	9½	9½	9	9.0
45	Prussian blue W. I.	8	9½	8½	8½	8.5
48	Ultramarine blue	—	—	—	—	—
49	Zinc and lead chromate	10	9½	10	9½	9.7
51	Magnetic black oxide	9	9½	10	9½	9.5
111	Brom composite paint	7	9	9	9	8.5
222	Black composite paint	9	9	9	8½	8.8
3333	White composite paint	4	4	7	3	4.5
444	Green composite paint	5	7	7	8	6.7
555	Black composite paint	9	9	6	9	8.2
666	Brown composite paint	8	8	6	9	7.7
777	White composite paint	7	10	5	7	7.2
888	Green composite paint	7	8	8	9	8.0
2000	1 coat zinc chromate 1 coat iron oxide excluder	8	8½	8	8	8.1
3000	1 coat lead chromate	7	8	7½	7½	7.3
4000	1 coat red lead 1 coat iron oxide excluder	7	8½	8	7½	7.7
100	Straight carbon black paint with turps and drier	5	8½	4	8½	6.5
90	Straight lampblack paint with turps and drier	5	7	3	8	5.7
5555	Coal tar paint over red lead	4	8	2	7	5.2
1000	Chrome resinate in oil (1 coat)	1	—	—	2	0.7
1 plate	3 coats boiled linseed oil	1	—	1	4	1.5

[10] Drugs, Oils and Paints (Phila.), XXIII, 4, 135 (1907).

pigments in prime coats which are of a metallic nature or which are good conductors of electricity should be avoided, owing to the danger of stimulating galvanic activity, the paint pigments constituting the cathode and the iron beneath acting as the anode, providing moisture penetrates the coating.

ATLANTIC CITY STEEL TEST PANELS.

It has already been stated above that as a result of the water-pigment tests which have been described it was decided to erect at Atlantic City a series of steel panels to be painted with the various pigments ground in a standard vehicle. These tests were under the supervision of Committee A—5 of the American Society for Testing Materials, and were carried out in a thoroughly practical manner and on a large scale.

Several official inspections of the Atlantic City Test Fence have been made since their erection. In each case the inspection has been made by a specially appointed sub-committee of experts. Space will not permit of a detailed account of each inspection that has been made. The results of the official inspection made in June, 1911, are however, included herewith in the following table. The scale of excellence and durability is given in figures ranging from 1 to 10, the latter figure being the highest rating.

A complete history of the Atlantic City steel test panels has recently been published and is available in book form.[12]

In Table No. 1, there is shown the rating accorded by each inspector to each panel, as well as an average for each panel.

In Table No. 2 there is shown the rating obtained by those panels which were considered by the committee as meriting from 8 to 10, and having given the best all-round service.

TABLE NO. 2.—ANALYSIS OF AVERAGES. GRADE OF EXCELLENCE FROM 8 TO 10.

Plate.	Pigment.	Average.
34	American vermilion (basis chromate of lead)..	10.0
41	Chrome green	9.8
49	Lead and zinc chromate.....	9.7
39	Zinc chromate	9.5
40	Zinc and barium chromate.....	9.5
51	Black oxide of iron.....	9.5
4	Sublimed white lead.....	9.0
44	Prussian blue I.....	9.0
5	Sublimed blue lead.....	8.8
20	Willow charcoal	8.8
222	Composite paint	8.8
45	Prussian blue II.....	8.5
111	Composite formula	8.5
9	Orange mineral	8.3
10	Red lead	8.3
555	Composite paint	8.2
12	Bright red oxide of iron.....	8.1
2000	1 coat zinc chromate; 1 coat iron oxide.....	8.1
14	Venetian red	8.0
888	Composite paint	8.0

Comparison of Results.—It is of interest to compare with Table 2 of the above report, Table 2 of the 1910 report of committee A—5 of the American Society for Testing Materials. Both charts show a large majority of the highly inhibitive pigments to be in the lead.

ANALYSIS OF AVERAGES. GRADE OF EXCELLENCE FROM 8 TO 10.

No.	Pigment.	Average.
34	American vermilion (chrome scarlet).....	9.8
41	Chrome green (blue tone).....	9.7
40	Zinc and barium chromate.....	9.7
5	Sublimed blue lead.....	9.6
4	Sublimed white lead.....	9.5
49	Zinc and lead chromate.....	9.5
39	Zinc chromate	9.4
12	Bright red oxide.....	9.3
44	Prussian blue	9.2
16	Natural graphite	9.1
9	Orange mineral (American).....	9.0
36	Medium chrome yellow.....	9.0
2	White lead (Quick process).....	8.9
20	Willow charcoal	8.8
45	Prussian blue II.....	8.8
1	White lead (Dutch process).....	8.7
10	Red lead	8.7
7	Zinc lead white.....	8.0

Present Appearance of Steel Panels.—A recent inspection of the plates showed that the corroded white lead films have chalked to a considerable extent and show heavy rusting. The zinc films have checked and crocked badly. The sublimed white lead and sublimed blue lead films were in good condition and indicated the value of such basic pigments as protectives of steel. The red lead films which have given good protection to the metal to which they were applied, showed a slight surface coating of carbonate of lead, due to the action of the carbonic acid of the atmosphere. The iron oxide films were all in very fair condition. The graphite and carbon black paints were shown to be pitted in several places, with excrescence of rust. The inert pigments, such as barytes, whiting, silica, and asbestine, gave very fair service for a short time, and then decay progressed quite rapidly in most cases. The plates painted with the chromate pigments were in most excellent condition in nearly every case. This was especially true of the plates painted with zinc chromate, basic lead chromate (American vermilion), and chrome green, the surfaces of these paints not having visibly chalked, checked, or disintegrated, and freedom from corrosion being shown throughout the test.

HAVRE DE GRACE TEST.

During 1906 a series of 57 commercial paints as found upon the American market, were carefully applied to steel test panels placed upon the Pennsylvania Bridge over the Susquehanna River, at Havre de Grace, Md. These tests were made under the auspices of Committee D—1 of the American Society for Testing Materials. The composition of the paints was unknown until they were analyzed subsequent to their application, by members of the committee.[13] The results of the analyses showed that the paints were made from a very wide range of pigments and vehicles, most of them being combinations of several types of pigments, oils, varnishes, and thinners. Some of the paints were applied over specially designed priming coats, while others were used without variation in the different coats. The same paints applied to the panels were also applied to sections of the bridge.

Inspections of the panels were made yearly, and have been reported from time to time, the first com-

[11] J. Newton Friend. The Corrosion of Iron and Steel, p. 208. Longmans, Green & Co., London (1911).

[12] H. A. Gardner. Paint Technology and Tests. McGraw-Hill Book Co. (1911). P. 220.

[13] Proc. Am. Soc. Testing Materials, VIII, 165 (1908).

plete inspection to report the condition of each individual panel was made in 1911.[14] The results of this inspection seemed to indicate that with one exception there is no very marked difference in the condition of the painted surfaces, most of which are showing very fair service, considering the time of exposure. The exception noted is a paint made of 100 per cent carbon pigments, and numbered 15 in the test. The very low rating accorded this panel was the result of the unanimous opinion of the inspectors. The only other paints in the tests containing 100 per cent of any pigment, were Nos. 10 and 11 in both of which pigment was red lead. Both of these paints have appeared in very good condition at each inspection, and received at the last inspection a high average rating.

The results of the Havre de Grace tests have been reported to the American Society for Testing Materials, and the reports have been published in the Proceedings so that it is not necessary to give them at this time. It may be stated that the preparation of the surfaces and the painting of all the panels on the Havre de Grace tests was very carefully done, which probably accounts for the high average of service which has been noted in these tests.

PAINT VEHICLES AND THEIR EXCLUDING VALUE.

The recent shortage of the flax crop and the consequent rise in price of linseed oil, has resulted in an attempt on the part of the manufacturer to utilize other oils which are of a slow drying or semi-drying nature. A most elaborate series of paint exposure tests upon various oils, is being conducted at the present time, on the grounds of The Institute of Industrial Research, at Washington. Until conclusive results are shown from these tests, it is probable that linseed oil will continue to be used as the vehicle for the highest grade paints. One mixture, however, that has shown well under test is composed of heavy blown linseed oil and soya bean oil in equal proportions. In certain cases the addition of China wood oil to linseed oil gives a glossier and harder film and it has been claimed that the addition of menhaden oil is advisable when the paints are to be exposed under moist and damp conditions, the percentage of stearates present in the marine animal oil acting as a moisture excluder. In this connection, Friend[15] has lately stated that the addition of one-half of one per cent of paraffine to a paint oil, gives to that oil rather remarkable water-resisting properties. In his tests he prepared a series of films from such an oil and found that their excluding value was 50 per cent higher than the excluding value of films not containing paraffine. As a matter of fact, paraffine, carnauba wax, and other water-resisting materials of this type have been used for several years in the United States, in the manufacture of paints for the protection of iron and steel. The results of Friend's research, therefore, are simply to corroborate the present practice among certain manufacturers. Some authorities, however, claim that paints containing wax are dangerous to use on account of the flat condition which they present upon drying, and the soft film which results when they are exposed to heat. Friend's monograph sums up the results of his investigations as follows:

A paint suitable for the protection of metal work should be composed of a suitable pigment in intimate association with a liquid vehicle excelling in the following particulars:

1 Chemical permanence.
2 Chemical inertness toward iron.
3 Resistance toward physical damage.
4 Imperviousness toward air and moisture.
5 Elasticity.

While we may safely admit these conclusions, the researches of the last few years seem to indicate that we should include another heading, perhaps the most important of all; namely, the inhibitive value of the pigment, for if this point is given attention the importance of the other qualifications is to some extent minimized. Slight openings or abrasions of the protective coatings are necessarily of less importance if a rust inhibitive action is provided by the pigmentary portion of the vehicle.

The only other work your reporter has been able to find worthy of record is the experimental work done by the United States Navy Department on paints for ship's bottoms. In view of the fact that practically no paint oil is used in the present specifications, this is a matter of interest.[16] The paint consists of a varnish vehicle of shellac in alcohol, with the addition of small percentages of turpentine and pine-tar oil. The pigment for the anticorrosive consists of dry metallic zinc dust and dry white zinc oxide, the exact ingredients for making 10 gal. of the anticorrosive paint being as follows:

7¼ gals. grain alcohol.
7 9/10 lbs. gum shellac.
3/5 gal. turpentine.
3/5 gal. pine-tar oil.
9½ lbs. metallic zinc, dry.
28½ lbs. white zinc oxide, dry.

The pigment for the antifouling paint consists of dry white zinc oxide, Indian red and red oxide of mercury, the exact ingredients for making 10 gal. of antifouling paint being as follows:

6 gals. grain alcohol.
13¾ lbs. gum shellac.
1 gal. pine-tar oil.
1 gal. turpentine.
13¾ lbs. white zinc oxide, dry.
13¾ lbs. Indian red.
4¾ lbs. red oxide of mercury, dry.

It is stated that at the fall docking of 1909 of the battleship fleet these paint formulas were found to have given good results with the usual types of paints.

The coal production in the United States in 1912, according to the Geological Survey, was 550,000,000 tons, surpassing the previous high record of 1910 by 10 per cent, and over double the production of 1900.

[14] Proceeding Am. Soc. for Testing Materials (1911).
[15] Iron and Steel Inst. Carnegie Scholarship Memoirs, VII, 1 (1911).
[16] United States Naval Institute Proceedings No. 138 (June, 1911), Vol. 37, No. 2.

METHODS OF ANALYSIS USED IN THE LABORATORIES OF THE ARMOUR INSTITUTE OF TECHNOLOGY.

Analysis of Brasses and Bronzes.

The sample is cut in small chips either by milling or drilling. In case the constituents of the alloy are unknown, it is best to run a good qualitative analysis to save time on later operations.

A 1.0 gram sample of the alloy is decomposed with strong nitric acid until the precipitated oxides are entirely free from dark spots. In case the time required is too long, a little strong HCl may be added and the acids completely evaporated. The salts are taken up with strong nitric and filtered. The residue of mixed oxides is washed by decantation with hot nitric acid (1:1), filtered through asbestos in a Gooch crucible. After washing thoroughly with nitric acid, the asbestos and mixed oxides are transferred to a beaker and heated gently with concentrated hydrochloric acid until the oxides are in solution. The solution is filtered through asbestos in a Gooch crucible to remove the asbestos, and after washing thoroughly with warm dilute hydrochloric acid the solution is ready for the separation of antimony and tin, with part of the iron.

The solution is cooled somewhat, the beaker covered with a watch-glass, and a hot solution of 15 gms. pure recrystallized oxalic acid is cautiously added (5 gms. for 0.1 gm. of the mixed oxides). This causes the evolution of considerable carbon dioxide. Now, in order to completely remove the excess of hydrogen peroxide the solution is boiled vigorously for ten minutes. The volume of the liquid should amount to from 80 to 100 c.c. After this a rapid stream of hydrogen sulphide is conducted into the boiling solution, and for some time there will be no precipitation, but only a white turbidity formed. At the end of five or ten minutes the solution becomes orange colored and the antimony begins to precipitate, and from this point the time is taken. At the end of fifteen minutes the solution is diluted with hot water to a volume of 250 c.c., at the end of another fifteen minutes the flame is removed, and ten minutes later the current of hydrogen sulphide is stopped. The precipitated antimony sulphide is filtered through a weighed Gooch crucible containing an asbestos mat. The precipitate is washed twice by decantation with 1 per cent oxalic acid and twice with very dilute acetic acid. Both of these wash liquids should be hot and saturated with hydrogen sulphide.

The crucible, with its contents, is placed in the front of the muffle furnace and ignited at a low temperature. It is then cooled and the antimony weighed as Sb_2O_4. Weight $\times$ 0.7898 = antimony.

The filtrate from the antimony sulphide is made acid with sulphuric acid and evaporated in a large porcelain or silica dish to fumes of SO_3. It is then cooled, diluted to 200 c.c., heated to 80° C. and hydrogen sulphide passed until the precipitate settles clear. Some of the clear liquid is then diluted with water and hydrogen sulphide passed through again. If no precipitate ensues, all of the tin has been converted to sulphide and may be filtered off on paper. If a precipitate ensues, the entire solution is diluted and hydrogen sulphide is passed until the clear solution, on dilution shows no further precipitate when hydrogen sulphide is passed. The tin sulphide is then filtered off, washed with a 10 per cent solution of ammonium nitrate dried, and ignited in porcelain. A small lump of ammonium carbonate is added and the crucible, with contents reheated over a Meker burner. The tin is then weighed as SnO_2. Weight $\times$ 0.7881 = tin.

The filtrate from the mixed oxides is evaporated to fumes with 10 to 15 c.c. concentrated H_2SO_4. If lead is found to be present, the solution is cooled and diluted to about 125 c.c. Alcohol, 20 to 25 c.c., is added and the solution allowed to stand about a half hour. The lead sulphate is filtered on asbestos in a Gooch crucible washed with 8 per cent sulphuric acid, dried, gently ignited, and weighed as $PbSO_4$. Weight $\times$ 0.6829 = lead.

The filtrate from the lead is combined with the filtrate from the tin after the latter has been boiled to expel H_2S then the mixture treated with excess H_2SO_3 till a strong smell of SO_2 is evident, heated to boiling and a slight excess of KI solution added. The heating is continued a few moments, the precipitate of CuI filtered on asbestos in a Gooch crucible washed with hot water and at the last a few c.c. of alcohol, dried at 105° and weighed as CuI. Weight $\times$ 0.3339 = Cu.

The filtrate from the copper is then boiled to remove sulphurous acid, and made faintly alkaline with ammonia. The excess ammonia should be boiled off and the precipitate, if any, filtered off. This will contain any aluminum, iron, and also bismuth if present.

These, if mixed together, may be separated by the regular quantitative methods, but usually, only one, iron, is present and may be weighed as Fe_2O_3. Weight $\times$ 0.6996 = iron.

The filtrate from above is made neutral with nitric acid, with litmus as indicator and excess sodium ammonium phosphate solution added. The flocculent precipitate which comes down at first changes on boiling to the granular zinc ammonium phosphate which may

be filtered readily on a Gooch washed with hot water, dried, ignited and weighed as $Zn_2P_2O_7$. Weight × 0.4291 = zinc.

Arsenic in small quantities may be determined in the filtrate from the zinc by making acid with HCl and saturating with H_2S. The sulphide is filtered off and washed with a little hydrogen sulphide water. It is then dissolved in dilute HCl which has been heated with $KClO_3$. The solution is made faintly alkaline with ammonia and the excess chlorine and hydrogen sulphide boiled off. Magnesia mixture is then added, the solution well agitated, excess ammonia added, and the whole mixture allowed to stand. It is then filtered on a Gooch, dried, and gently ignited. It is weighed as $Mg_2 As_2 O_7$ and the arsenic calculated. Weight × 0.4827 = arsenic.

THE VISCOSITY OF LUBRICATING OILS.*

By A. E. DUNSTAN, D.Sc., and J. F. STREVENS.

At the Seventh International Congress of Applied Chemistry, London, 1909, one of the present authors foreshadowed the more extensive application of viscosity as a valuable constitutive property, not only because of its specific suitability as a criterion of lubricating efficiency, but also as a means of determining adulteration, and checking purity. It is, indeed, a matter for astonishment that a property which varies within such wide limits for individual substances and which, with properly designed apparatus, is so susceptible to accurate measurement, should have met with relatively little application in technical chemistry. In this communication, which deals more particularly with the connection between lubrication and viscosity, the authors desire to advance the proposition that the viscosity of a lubricating oil can only be satisfactorily dealt with in the form of a temperature curve, so that the behavior of an oil can be approximately predicted if the working conditions are known. Further, they wish to point out that the viscosity of an oil should be expressed in absolute units of dynes per square centimetre, so that all oils may be directly compared, and lastly that the apparatus in which the bulk of the purely scientific work on viscosity has been carried out is eminently suitable for technical purposes. It is obvious, of course, that any standard oil may be taken for comparison purposes, and the results quoted as they are at present, in terms of such an oil.

APPARATUS AND METHOD.

The simple apparatus devised by Ostwald is, in point of fact, a modification of that used by Poiseulle a century ago in his classical investigations on viscosity. A reference to Fig. 1 will show the chief points of the viscometer.

Filtered oil is run into the viscometer to the marks c d. It is now suspended in a bath of paraffin wax or suitable clear high flash oil. It is adjusted quite vertically by reference to plumb lines suspended in the bath. A two-litre Jena beaker forms a convenient bath, and stirring may be carried out by means of a glass paddle, run off a hot air motor. A delicate thermometer is immersed in the bath. If the determinations are carried out in a suitable place, well shielded from draughts of air, surprisingly steady temperatures may be maintained for long intervals. It is advisable, however, to guard the apparatus with asbestos millboard, as a protection against temperature fluctuations. After the viscometer has been immersed 15 minutes at constant temperature, the levels of the oil should be accurately adjusted to the marks c-d, by means of a warmed glass pipette. Rubber tubing is fixed to the top of bulb A, and the oil slowly sucked up above mark a. It is then allowed to flow down, and when the meniscus passes "a," a stop-watch reading to fifth seconds is started and the time of flow between a and b is taken. Four or five determinations are made and averaged. For ordinary oils the following dimensions will be found useful: Capillary, C, 6 cms. by 1 mm. bore; bulb A, 4 c.c., bulb B, 8 c.c.; length over all 15 cms.

For lubricating oils it is advisable to take a series of

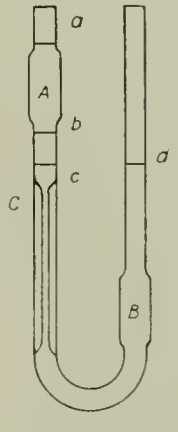

Fig. 1.

readings between 70° C. and 200° C., when a curve may be plotted, giving in a graphic form the variation of viscosity with temperature. The method of calculation is as follows: The viscometer must be accurately known as a range of temperature: moreover, this standard liquid must be very viscous. Phenol is very suitable for this purpose, since its viscosity has been determined independently by Scarpa, Dunstan and Thole.

VISCOSITY OF PURE PHENOL.

Temperature.	Observer.	Viscosity.
25	Scarpa	0.0850
45	Thole	0.0404
50	Dunstan	0.0337
60	Dunstan	0.0253
70	Scarpa	0.0197

Suppose the time of flow of phenol in the given viscometer was seconds. Then viscosity = K × time × density, where K is a constant for the particular instrument. It will be found that K only varies slightly with temperature, and the values for K lie evenly on

*From the Journal of the Society of Chemical Industry.

a straight line which forms the calibration curve for the viscometer.

To take an actual example: Temp. = 73.5 C.; t = 130.5 secs.; log K for viscometer = 3.0414; specific gravity of oil = 0.877.

Then viscosity = K × t × d = 0.126.

EXPERIMENTAL RESULTS.

Medium spindle oil.		Light marine engine oil.	
Temp. °C.	Viscosity.	Temp. °C.	Viscosity.
64°	0.110	70°	0.230
100°	0.0348	100°	0.0780
150°	0.0123	140°	0.0246
		150°	0.0196
Heavy Texas engine oil.		Ravison rape oil.	
70°	0.181	70°	0.146
110°	0.0454	100°	0.0673
150°	0.0175	130°	0.0327
		150°	0.0219
Standard cylinder oil.		Bayonne medium gas engine oil.	
70°	0.951	70°	0.148
100°	0.263	100°	0.0550
150°	0.0361	150°	0.0157
190°	0.0237		
198°	0.0187		
Medium gas engine oil.		Galician engine oil.	
70°	0.148	75°	0.198
100°	0.0550	100°	0.0638
150°	0.0157	125°	0.0319
Russian engine oil.		Price's A air-cooled motor oil.	
80°	0.122	80°	0.368
100°	0.0535	130°	0.0684
150°	0.0160	170°	0.0240
Locomotive cylinder oil.		A crude American unrefined oil.	
80°	0.660	80°	0.162
100°	0.279	115°	0.053
150°	0.0574	150°	0.0216
180°	0.0265	170°	0.0139
Elektrion rape oil.			
120°	0.694		
150°	0.274		
180°	0.111		

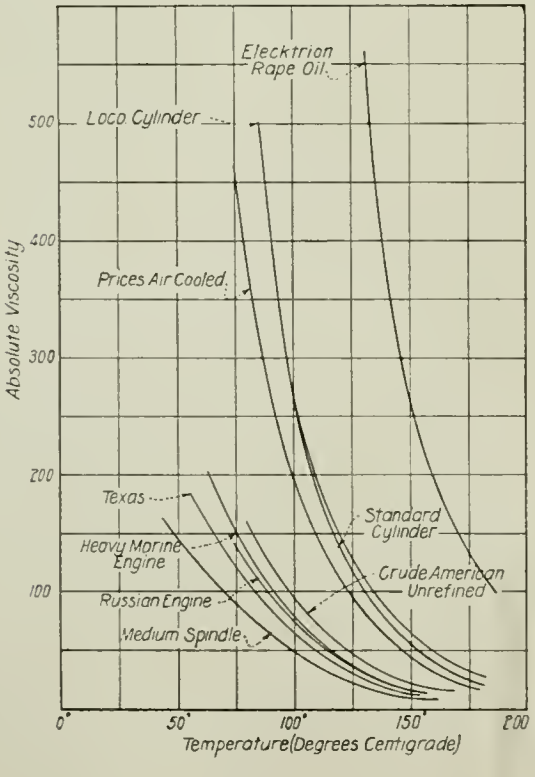

Fig. 2.

The specific gravities are best determined in a narrow-necked 10 c.c. flask, provided with an etched mark. The oil is adjusted to the mark with a fine pipette after 15 minutes' immersion. The temperature correction for expansion of glass may be determined by finding the weight of water contained in it at various temperatures and constructing a correction curve.

No viscosity determination can exactly reproduce the actual conditions under which the lubricating oil will be used, and consequently the above results are of an arbitrary nature. Still, undoubtedly it would be of value, when dealing with a given oil, to plot its viscosity curve and compare it with one afforded by an oil of real merit. The more viscous the lubricant becomes, the stronger is the adhesion between it and the bearings, and the greater the pressure and temperature it will sustain, but excessive viscosity causes unnecessary friction, so that the ideal lubricant has just the correct viscosity to keep the moving surfaces apart under the working conditions. It follows, then, that some knowledge, at least approximate, must be had of the maximum temperature to which the oil will be subjected, and it is apparent from the curves that above 200 C., although the viscosities tend to approximate, they still are widely different for light engine oils and heavy cylinder oils. The authors are attempting to carry their method out at still greater temperatures, but consider that they have made out a good case for the study of viscosity temperature curves.

According to a report of the Secretary of the Interior for the fiscal year ending June 30, 1912, the United States Patent Office received during the year 69,236 applications for mechanical patents, 1,775 for designs, 195 for reissues, 7,238 for trade marks, 941 for labels and 362 for prints. There were 35,539 patents granted, including reissues and designs, and 4,635 trade marks, 625 labels and 268 prints were registered. The number of patents that expired was 19,634, and 6,970 allowed applications were forfeited for non-payment of final fees. The total receipts of the office were $2,094,059.50; the total expenditures $2,019,236.01, and the net surplus, $74,823.49. The total net surplus of receipts over expenditures is now $7,138,749.25. The figures show a material increase of business over the previous year, and the report recommends the providing of a new building for the Patent Office, the capacity of the present one being taxed to its limit. The models have had to be removed to the basement of the House Office building, where they are practically inaccessible to the Patent Office, and it has been necessary to store valuable records in the hallways, where they are exposed to dust and the ravages of time, as well as danger of destruction by fire. The office has earned a sufficient sum to purchase land for a new building opposite the Capitol and north of the Library of Congress, and the Commissioner of Patents recommends that this land be bought. He also recommends that legislation be enacted for the protection of collective trade marks for industrial property.

METALLURGY.

THE NOMENCLATURE OF THE MICROSCOPIC SUBSTANCES AND STRUCTURES OF STEEL AND CAST IRON.

At the 6th Congress of the International Association for Testing Material, the committee in charge of the subject indicated by the title of this article submitted its report. The committee for studying this problem is constituted as follows: Prof. H. M. Howe, New York, chairman; Prof. Albert Sauver, Boston, secretary; members: F. Osmond, Paris; Dr. H. C. H. Carpenter, Manchester; Prof. W. Campbell, New York; Prof. C. Benedicks, Stockholm; Prof. F. Wüst, Aachen; Prof. A. Stansfield, Montreal; Dr. J. E. Stead, Middlesborough; Prof. L. Guillet, Paris; Prof. E. Heyn, Berlin-Lichterfelde; Dr. W. Rosenhain, Teddington. In submitting its report the committee stated that:

The theoretical matter in this report is given solely by exposition and the committee disclaims the intent to impose any theory. This report is offered for adoption subject to this disclaimed on the ground that the adoption of theories is beyond the powers of a Congress.

The report of the committee was as follows:

I. GENERAL PLAN.

We first enumerate the substances of such importance as to warrant it, indicating roughly their constitution, and then define and describe certain of them.

The conditions which we meet are (1) that we need definitions on which all can agree; and this implies that they must be free from all contentious matter, and be based on what all admit to be true. (2) That the reader must needs know the current theories as to the constitution of these substances, and these theories are necessarily contentious. We meet these conditions by the plan of giving (1), the Name which we recommend for general use, followed immediately in parentheses by the other names used widely enough to justify recording them; (2) the Definition proper, based on an undisputed quality, e. g. that of austenite which we base on its being an iron-carbon solid solution, purposely omitting all reference to the precise nature of solvent and solute; and (3) Constitution, etc., etc., in which we give the current theories as to the nature of solvent and solute and appropriate descriptive matter.

The distinction between these three parts should be understood. (1) The Names actually used are matter of record and indisputable. (2) The Definitions are matters of convention or treaty, binding on the contracting parties, though subject to denouncement, preferably based on some determinable property of the thing defined as distinguished from any theory as to its nature, or if necessarily based on any theory it should be a theory which is universally accepted. It is a matter purely of convention and general convenience what individual property of the thing defined shall form the basis of the definition. The name and the definition should endure permanently, except in the case of a definition based on an accepted theory, which must be changed if the theory should later be disproved. (3) Theories and Descriptions are not matters of agreement or convention but dependent on observation, and therefore always subject to be changed by new discoveries. They are temporary in their nature, as distinguished from the names and definitions which should be fixed, at least relatively.

This case of austenite illustrates the advantages of non-indicative names. The names which we propose to displace, "gamma iron" and "mixed crystals," imply definite theories as to the nature of austenite, and hence might have to be abandoned in case those theories were later disproved. The name "austenite" implies nothing, like mineralogical names in general, and hence is stable in itself. Our infant branch of science may well learn from its elder sister, which has tried and proved the advantage of this non-indicative naming.

In those cases in which a name has been used in more than one sense we advise the retention of one and the abandonment of the others, having obtained the consent of the proposers of such names for their abandonment.

Many of whose judgment we respect object to our including certain of the less used names, e. g. from i to n in our list, holding them either to be confusing or to be needless.

It is true that several names (hardenite, martensite, sorbite, etc.), have been used with various meanings, and hence confusingly, in spite of which most of them should be retained, each with a single sharp-cut definition, because they are so useful.

As regards the alleged needlessness of certain names it is for each writer to decide whether he does or does not need names with nice shades of meaning, such as osmondite and troostosorbite. Those who look only at the general outlines and not at the details have no right to forbid the workers in detail from having and using words fitting their work; nor have those whose needs are satisfied by the three primary colors a right to forbid painters, dyers, weavers, and others from naming the many shades with which they are concerned. Like the lexicographer we must serve the reader by explaining those words which he will meet, whether we individually use or condemn them. We feel that we have exhausted our powers in cautioning writers that certain words are rare and not likely to

be understood by most readers, or are improper for any reason, and in urging the complete abandonment of those withdrawn by their proposers.

Needless words will die a natural death; needed ones we cannot kill. The good we might do in hastening the death of the moribund by omitting them from this report is less than the good we do by teaching their meaning to those who will meet them in antemortem print. These readers have rights. We serve no class, but the whole.

Illustrations. At the end of the several descriptions the reader is referred to good illustrations in Osmond and Stead's Microscopic Analysis of Metals, Griffin & Co., London, 1904.

II. LIST OF MICROSCOPIC SUBSTANCES.

The microscopic substances here described consist of

1. Metarals, true phases, like the minerals of nature. These are either elements, definite chemical compounds, or solid solutions, and hence consisting of definite substances in varying proportions. These include austenite, ferrite, cementite, and graphite.

2. Aggregates, like the petrographic entities as distinguished from the true minerals. These mixtures may be in definite proportions, i. e. eutectic, or eutectoid mixtures, (ledeburite, pearlite, steadite) or in indefinite proportions (troostite, sorbite). Those aggregates which are important for any reason are here described.

(Many true minerals, such as mica, felspar, and hornblende, are divisible into several different species so that these true mineral names may be either generic or specific. These genera and species are definite chemical compounds, in which one element may replace another. Other minerals, such as obsidian, are solid solutions in varying proportions, and in these also one element may replace another. Metarals like minerals differ from aggregates in being severally chemically homogeneous).

These two classes may be cross classified into:

(A) The iron-carbon series, which come into being in cooling and heating.

(B) The important impurities, manganese sulphide, ferrous sulphide, slag, etc.

(C) Other substances.

The most prominent members of the iron-carbon series are

I. Molten iron, metaral, molten solution, but hardly a microscopic constituent.

II. The components which form in its solidification:

(a) Austenite, solid solution of carbon or iron carbide in iron, metaral;

(b) Cementite, definite metaral, Fe_3C;

(c) Graphite, definite metaral, C.

III. The transition substances which form through the transformation of austenite during cooling:

(d) Martensite, metaral of variable constitution; its nature is in dispute;

(e) Troostite, indefinite aggregate, uncoagulated mixture;

(f) Sorbite, indefinite aggregate, chiefly uncoagulated pearlite plus ferrite or cementite;

IV. Products* of the transformation of austenite:

(g) Ferrite;

(h) Pearlite.

This transformation may also yield cementite and graphite as end products in addition to those under b and c.

In addition to the above, the names of which are universally recognized and in general use, the following names have been used more or less:

(i) Ledeburite (Wüst), definite aggregate, the austenite-cementite eutectic:

(j) Ferronite (Benedicks) hypothetical definite metaral, β iron containing about 0.27 per cent of carbon;

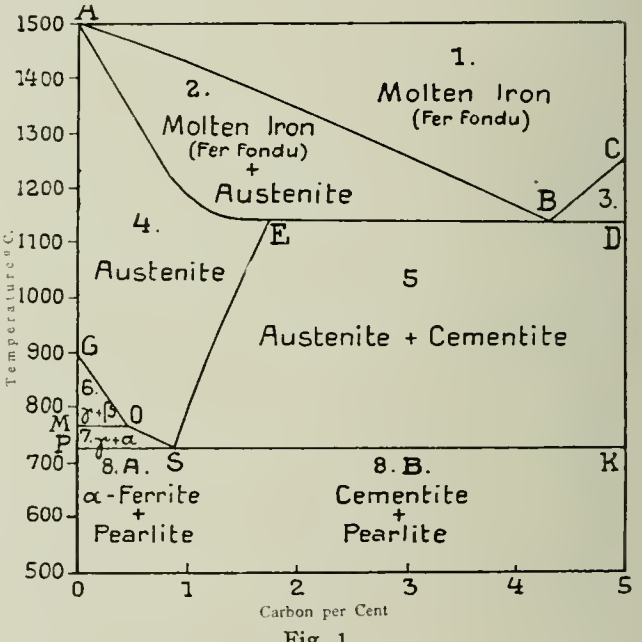

Fig. 1.

The line PSK is often called "A1." The line GOS is often called "A3," and this name is sometimes applied to the line SE.

(k) Steadite (Sauveur) definite aggregate, the iron-phosphorus eutectic (rare);

And three transition stages in the transformation of austenite, viz.:

(l) Hardenite (Arnold) collective name for the austenite and martensite of eutectoid composition;

(m) Osmondite (Heyn) boundary stage between troostite and sorbite;

(n) Troosto-sorbite (Kourbatoff) indefinite aggregate, the troostite and the sorbite which lie near the boundary which separates these two aggregates; (obsolescent).

III. DEFINITIONS AND DESCRIPTIONS.

Carbon iron equilibrium diagram, Fig. 1. Under the several substances about to be described an indication will be given of the parts of the carbon iron

*In hypo-eutectoid steels these habitually play the part of end products, though, according to the belief of most, the true end of the transformation is not reached till the whole has changed into a conglomerate of ferrite plus graphite.

equilibrium diagram, Fig. 1, to which they severally correspond.

Austenite. Osmond (Fr. Austenite, Ger. Austenit called also mixed crystals and gamma iron. Up to the year 1900 often called martensite, and wrongly sometimes still so called). Metaral of variable composition.

Definition: The iron-carbon solid solution as it exists above the transformation range or as preserved with but moderate transformation at lower temperatures, e. g. by rapid cooling, or by the presence of retarding elements (Mn, Ni, etc.), as in 12 per cent manganese steel and 25 per cent nickel steel.

Constitution and Composition. A solid solution of carbon or iron carbide (probably Fe_3C) and gamma iron, normally stable only above the line PSK of the carbon iron diagram. It may have any carbon content up to saturation as shown by the line SE, viz.: about 0.90 per cent at S (about 725° C.) to 1.7 per cent at E (about 1130°). The theory that the iron and the carbide or carbon, instead of being dissolved in each other, are dissolved in a third substance, the solution of eutectic composition ($Fe_{24}C$, called hardenite) is not in accord with the generally accepted theory of the constitution of solutions, and is not entertained widely or by any member of this committee.

Crystallization. Isometric: The idiomorphic vug crystals are octahedra much elongated by parallel growth. The etched sections show much twinning. (Osmond and most authorities.) Le Chatelier believes it to be rhombohedral. Cleavage octahedral.

Varieties and Genesis: 1. Primary austenite formed in the solidification of carbon steel and hypo-eutectic cast iron; 2. Eutectic austenite, interstratified with eutectic cementite, making up the eutectic formed at the end of the solidification of steel containing more than about 1.7 per cent of carbon, and of all cast iron.

Equilibrium: It is normal and in equilibrium in Region 4, and also associated with beta iron in Region 6, with α iron in Region 7, and with cementite in Region 5. It should normally transform into pearlite with either ferrite or cementite on cooling past A1 into Region 8.

Transformation: In cooling slowly through the transformation range, Ar3—Ar1, austenite shifts its carbon content spontaneously through generating pro-eutectoid ferrite or cementite, to the eutectoid ratio, about 0.90 per cent, and then transforms with increase of volume at Ar1 into pearlite, q. v., with which the ejected ferrite or cementite remains mixed. Rapid cooling and the presence of carbon, manganese, and nickel obstruct this transformation, (1) retarding it and (2) lowering the temperature at which it actually occurs, and in addition (3) manganese and nickel lower the temperature at which in equilibrium it is due. Hence by combining these four obstructing agents in proper proportions the transformation may be arrested at any of the intermediate stages, martensite, troosite, or sorbite*), q. v., and if arrested in an earlier stage, it can be brought to any later desired stage by a regulated reheating or "tempering." For instance, though a very rapid cooling in the absence of the three obstructing elements checks the transformation but little and only temporarily, yet if aided by the presence of a little carbon it arrests the transformation wholly in the martensite stage; and in the presence of about 1.50 per cent of carbon such cooling retains about half the austenite so little altered that it is "considerably" softer than the usually darker needles of the surrounding martensite, with which it contrasts sharply. Again either (a) about 12 per cent of manganese plus 1 per cent of carbon, or (b) 25 per cent of nickel, lower and obstruct the transformation to such a degree that austenite persists in the cold apparently unaltered, even through a slow cooling. (Hadfield's manganese steel and 25 per cent nickel steel, manganiferous and niccoliferous austenite respectively.)

Occurrence: When alone (12 per cent manganese and 25 per cent nickel steel and Maurer's 2 per cent carbon plus 2 per cent manganese austenite) polyhedra, often coarse, much twinned at least in the presence of martensite, and readily developing slip bands. In hardened high-carbon steel it forms a ground mass pierced by zig-zag needles and lances of martensite.

Etching: All the common reagents darken it much more than cementite, less than troosite or sorbite, and usually less, though sometimes more than martensite, which is recognized by its zig-zag shape, and needle structure. With ferrite and pearlite it is never associated.

Physical Properties: Maurer's austenite of 2 per cent manganese plus 2 per cent carbon is but little harder than soft iron, and 25 per cent nickel steel and Hadfield's manganese steel are but moderately hard. Yet as usually preserved in hardened high carbon steel, the hardness of austenite does not fall very far short of that of the accompanying martensite, probably because partly transformed in cooling. (Osmond's (d) and (e) are grouped together as "free" or "mas-words are that it is "considerably" softer than that martensite.)

Specific Magnetism very slight unless perhaps in intense fields. In Hadfield's manganese steel and 25 per cent nickel steel, very ductile.

Illustrations: Microscopic Analysis of Metals, Figs. 20, 50 and 51, on pp. 39, 100 and 101.

Cementite (Sorby "intensely hard compound," Ger. Cementit, Fr. Cémentite, Arnold, crystallized normal carbide). Definite metaral.

Definition: Tri-ferrous carbide, Fe_3C. The name is extended by some writers so as to include tri-carbides in which part of the iron is replaced by manganese, or other elements. Such carbides may be called "manganiferous cementite," etc.

2. Occurrence: (a) Pearlitic, as a component of pearlite, q. v.; (b) eutectic; (c) primary or pro-eutectic; (d) pro-eutectoid; (e) that liberated by the splitting up of the eutectic or pearlite; and (f) uncoagu-

lated in sorbite, troosite, and perhaps martensite; (c), sive."

Primary cementite is generated in cooling through Region 3: eutectic cementite on cooling past the line EBD; pro-eutectoid cementite in cooling through Region 5; pearlite cementite on cooling past the line PSK, or A1. Though the several varieties of cementite are generally held to be all metastable, tending to break up into graphite plus either austenite above A1 or ferrite below A1, yet they have a considerable and often great degree of persistence. The graphitizing tendency is completely checked in the cold, but increases with the temperature, and with the proportion of carbon and of silicon present, and is opposed by the presence of manganese.

3. Crystallization: Orthorhombic, in plates.

4. Structure: (a) Pearlitic, in parallel unintersecting plates alternating with plates of ferrite; (b) Eutectic, plates forming a network filled with a fine conglomerate of pearlite with or without pro-eutectoid cementite; (c) Primary, in manganiferous white cast iron, etc., in rhombohedral plates; (d) In hyper-eutectoid steel, pro-eutectoid cementite forms primarily a network enclosing meshes of pearlite, through which cementite plates or spines sometimes shoot if the net work is coarse; (e) Cementite liberated from pearlite merges with any neighboring cementite; (f) The structure of uncoagulated cementite cannot be made out. On long heating the pro-eutectoid and pearlitic cementite spheroidize slowly, and neighboring particles merge; (g) In white irons rich in phosphorus in flat plates embedded in iron-carbon-phosphorus eutectic.

5. Etching, etc.: After polishing stands in relief. Brilliant white after etching with dilute hydrochloric or picric acid; darkened by boiling with solution of sodium picrate in excess of sodium hydrate.

6. Physical Properties: Hardest component of steel. Hardness = 6 of Mohs scale. Scratches glass and felspar but not quartz; very brittle. Specific magnetism about two-thirds that of pure iron.

Illustrations, Microscopic Analysis of Metals, Figs. 42, and 43 on pp. 84, 85.

Martensite (Fr. Martensite, Ger. Martensit), Metaral. Its nature is in dispute.

Definition: The early stage in the transformation of austenite characterized by needle structure and great hardness, as in hardened high-carbon steel.

Constitution: I. (Osmond and others), a solid solution like austenite, q. v., except that the iron is partly beta, whence its hardness, and partly alpha, whence its magnetism in mild fields. II. (Le Chatelier) the same except that its iron is essentially alpha, and the hardness due to the state of solid solution. III. (Arnold) a special structural condition of his "hardenite" (austenite); not widely held. IV. A solid solution in gamma iron. V. (Benedicks). The same as I, except that the iron is wholly beta, and that beta iron consists of alpha iron containing a definite quantity of gamma iron in solution.

Equilibrium: It is not in equilibrium in any part of the diagram, but represents a metastable condition in which the metal is caught during rapid cooling, in transit between the austenite condition stable above the line A1 and the condition of ferrite plus cementite into which the steel habitually passes on cooling slowly past the line A1.

Occurrence: The chief constituent of hardened carbon tool steels, and of medium nickel and manganese-steels. In still less fully transformed steels (1.50 per cent carbon steel rapidly quenched, etc.) it is associated with austenite; in more fully transformed ones (lower carbon steels hardened, high carbon steels oil hardened, or water hardened and slightly tempered, or hardened thick pieces even of high-carbon steel) it is associated with troostite, and with some pro-eutectoid ferrite or cementite, q. v., in hypo and hyper-eutectoid steels respectively. In tempering it first changes into troosite; at 350°—400° it passes through the stage of osmondite; at higher temperatures it changes into sorbite; and at 700° into granular pearlite. On heating into the transformation range this changes into austenite, which on cooling again yields lamellar pearlite.

Characteristic specimens are had by quenching bars 1 c.m. square of eutectoid steel, i. e. steel containing about 0.9 per cent of carbon in cold water from 800° C. (1472° F.).

Structure: When alone, habitually in flat plates made up of intersecting needles parallel to the sides of a triangle. When mixed with austenite, zig-zag needles, lances, and shafts.

If produced by quenching after heating to 735° C., it consists of minute crystallites resembling the globulites of Vogelsang, which are rarely arranged in triangular order. At times so fine as to suggest being amorphous.

Etching: With picric acid, iodine, or very dilute nitric acid etches usually darker than austenite, but sometimes lighter, always darker than ferrite and cementite, but always lighter than troosite.

Illustrations, Microscopic Analysis of Metals, Figs. 19, p. 38, Fig. 52 on p. 102.

Ferrite (Fr. Ferrite, Ger. Ferrit), definite metaral.

1. Definition: Free alpha-iron.

2. Composition: Nearly pure iron. It may contain a little phosphorus and silicon, but its carbon content if any is always small, at the most not more than 0.05 per cent, and perhaps never as much as 0.02 per cent.

3. Occurence: (a), pearlitic as a component of pearlite, q. v.: (b) pro-eutectoid ferrite generated in slow cooling through the transformation range; (c) that segregated from pearlite, i. e. set free by the splitting up of pearlite, especially in low carbon steel; (d) uncoagulated as in sorbite, and probably troostite; (b) and (c) are classed together as free or massive.

Thus ferrite is normal and stable in regions 7 and 8.

4. Crystallization: Isometric, in cubes or octahedra.

5. Structure: (a) Pearlitic ferrite, unintersecting parallel plates alternating with plates of cementite; (b) pro-eutectoid ferrite in low-carbon steel forms irregular polygons, each with uniform internal orientation. In higher carbon steel, after moderately slow cooling, especially in the presence of manganese, it forms a network enclosing meshes of pearlite. In slower cooling this network is replaced by irregular grains separated by pearlite; (c) the ferrite set free by the splitting up of pearlite merges with the pro-eutectoid ferrite if any; (d) the structure of the ferrite in sorbite, etc., cannot be made out.

6. Etching: Dilute alcoholic nitric or picric acid on light etching leaves the ferrite grains white with junctions which look dark. Deeper etching, by Heyn's reagent or its equivalent, reveals the different orientation of the crystals or grains, (a) as square figures parallel to the direction of the etched surface, (b) as plates which dip at varying angles and become dark or bright when the specimen is rotated under oblique illumination. Still deeper etching reveals the component cubes, (etching figures, Ätzfiguren), at least if the surface is nearly parallel to the cube faces.

7. Physical Properties: Soft; relatively weak (tenacity about 40,000 lbs. per sq. in.); very ductile; strongly ferro-magnetic; coercitive force very small.

Grain Size: For important purposes (1) etch deeply enough, e. g. with copper-ammonium chloride, to reveal clearly the junctions of the grains; (2) count on a photograph of small magnification the number of grains in a measured field so drawn as to exclude fragments of grains; after (3) determining the true grain boundaries by examination under high powers (Heyn's method). Deep nitric acid etching is inaccurte, because an apparent grain boundary may contain several grains.

Illustrations, Microscopic Analysis of Metals, Figs. 41, 56, pp. 79, 116.

Osmondite (Fr. Osmondite, Ger. Osmondit).

Definition: That stage in the transformation of austenite at which the solubility in dilute sulphuric acid reaches its maximum rapidity. Arbitrarily taken as the boundary between troostite and sorbite.

Earlier Definition: Defined by the Vth Congress as having the "maximum solubility in acids and by a maximum coloration under the action of acid metallographic reagents." The present definition is confined to maximum rapidity of dissolving, because we do not yet know that this in all cases co-exists with the maximum depth of coloration, and in any case in which these two should not co-exist, the old definition does not decide which is true osmondite.

Constitution: The following hypotheses have been suggested, none of which has firm experimental foundation. 1. A solid solution of carbon or an iron carbide in alpha iron. 2. The coloidal system of Benedicks in its purity, troostite being this system while forming at the expense of martensite, and sorbite, being this system coagulating and passing into pearlite. 3. The stage of maximum purity of amorphous alpha iron on the way to crystallizing into ferrite.

Occurrence: Hardened carbon steel of about 1 per cent of carbon when reheated (tempered) to 350—400° C. passes through the stage of troostite to that of osmondite, and on higher heating to that of sorbite. What variation if any from this temperature is needed to bring hardened steel of other carbon content to the osmondite stage is not known. In that it represents a true boundary state between troostite and sorbite it differs in meaning from troosto-sorbite which embraces both the troostite and the sorbite which lie near this boundary. Indeed osmondite has sometimes been used in this looser sense. Writers are cautioned that, however useful these terms may prove for making these nice discriminations, they are not likely to be familiar to general readers.

Etching: According to Heyn it differs from troostite and sorbite in being that stage in tempering which colors darkest on etching with alcoholic hydrochloric acid.

The present definition and description of osmondite should displace previous ones, because they have the express approval of Professor Heyn, the proposer of the name, and M. Osmond himself.

Ferronite (Fr. Ferronite, Ger. Ferronit) (Benedicks), hypothetical definte metaral.

Definition: Solid solution of about 0.27 per cent of carbon in beta iron.

Occurrence (hypothetical): In slowly cooled steels and cast iron containing 0.50 per cent of combined carbon or more, that which is generally believed to be ferrite, whether pearlitic or free, is supposed by Benedicks to be ferronite.

Hardenite (Fr. Hardenite, Ger. Hardenit).

Definition: Collective name for austenite and martensite of eutectoid composition. It includes such steel (1) when above the transformation range, and (2) when hardened by rapid cooling.

Observations: On the generally accepted theory that austenite is a solid solution of carbon or an iron carbide in iron, hardenite is the solution of the lowest transformation temperature, i. e. the eutectoid. The theory that instead it is a definite chemical compound, $Fe_{21}C$, is considered under Austenite. Its proposer includes under hardenite both eutectoid (0.90 per cent carbon) austenite when above the transformation range, and the martensite into which that austenite shifts in rapid cooling (hardening).

Other Meanings: Originally (Howe, 1888) collective name for austenite and martensite of any composition in carbon steel. Osmond (1897), austenite saturated with carbon. Both these meanings are withdrawn by their proposers.

Pearlite (Sorby's "pearly constituent." At first written "pearlyte," Fr. Perlite, Ger. Perlit). Aggregate.

Definition: The iron carbon eutectoid, consisting of alternate masses of ferrite and cementite.

Constitution and Composition: A conglomerate of about 6 parts of ferrite to 1 of cementite. When pure, contains about 0.90 per cent of carbon, 99.10 per cent of iron.

Occurrence: Results from the completion of the transformation of austenite brought spontaneously to the eutectoid carbon-content, and hence occurs in all carbon steels and cast iron containing combined carbon and cooled slowly through the transformation range, or held at temperatures in or but slightly below that range, long enough to enable the ferrite and cementite to coagulate into a mass microscopically resoluble. Hence it is the normal constituent in Region 8. Its ferrite is stable but its cementite is metastable and tends to transform into ferrite and graphite.

Varieties and Structure: Because pearlite is formed by the coagulation of the ferrite and cementite initially formed as the irresoluble emulsion, sorbite (Arnold's sorbitic pearlite), there are the indefinitely bounded stages of sorbitic pearlite (Arnold's normal pearlite), i. e. barely resoluble pearlite, in the border land between sorbite and laminated pearlite; granular pearlite, in which the cementite forms fine globules in a matrix of ferrite; and laminated or lamellar pearlite, consisting of fine, clearly defined, non-intersecting, parallel lamellae alternately of ferrite and cementite. The name granular pearlite was first used by Sauveur to represent what is now called sorbite. This meaning has been withdrawn.

An objection to Arnold's name "normal pearlite" is that it is likely to mislead. "Normal" here apparently refers to arising under normal conditions of cooling, but (1) it rather suggests structure normal for pearlite, which surely is the lamination characteristic of eutectics in general, and (2) the general reader has no clue as to what conditions of cooling are here called normal. Many readers are not manufacturers, and even in manufacture itself air cooling is normal for one branch and extremely slow furnace cooling for another. Arnold calls troostite "troostitic pearlite" and sorbite "sorbitic pearlite." This is contrary to general usage, which restricts pearlite to microscopically resoluble masses.

Etching: After etching with dilute alcoholic nitric or picric acid it is darker than ferrite or cementite but lighter than sorbite and troostite. A magnification of at least 250 diameters is usually needed for resolving it into its lamellae, though the pearlite of blister steel can often be resolved with a magnification of 25 diameters. The more rapidly pearlite is formed, the higher the magnification needed for resolving it.

Illustrations, lamellar pearlite. Osmond and Stead, Microscopic Analysis, Fig. 11, p. 19, Granular pearlite, idem Fig. 18, p. 36; Heyn and Bauer, Stahl und Eisen, 1906, Fig. 14, opposite p. 785.

Graphite (Ger. Graphit, Fr. Graphite), definite metaral.

Definition: The free elemental carbon which occurs in iron and steel.

Composition: Probably pure carbon, identical with native graphite.

Genesis: Derived in large part, and according to Goerens wholly, from the decomposition of solid cementite. Others hold that its formation as kish may be from solution in the molten metal, and that part of the formation of temper graphite may be from elemental carbon dissolved in austenite. It is the stable form of carbon in all parts of the diagram.

Occurrence: (1) as kish, flakes which rise to the surface of molten cast iron and usually escape thence; (2) as thin plates, usually curved, e. g., in gray cast iron, representing carbon which has separated during great mobility, i. e., near the melting range; (3) as temper graphite (Ger. Temperkohle, Ledebur) pulverulent carbon which separates from cementite and austenite, especially in the annealing process for making malleabilized castings.

Graphite and ferrite are sometimes associated in a way which suggests strongly that they represent a graphite-austenite eutectic. But the existence of such a true eutectic is doubted by most writers.

Properties: Hexagonal. H. 1—2. Gr. 2.255. Streak black and shining, luster metallic; macroscopic color, iron black to dark steel gray, but always black when seen in polished sections of iron or steel under the microscope; opaque; sectile; soils paper; flexible; feel, greasy.

Troostite (Fr. Troostite, Ger. Troostit). Probably aggregate. (Arnold, troostitic pearlite.)

Definition: In the transformation of austenite, the stage following martensite and preceding sorbite (and osmondite if this stage is recognized).

Constitution and consumption: An uncoagulated conglomerate of the transition stages. The degree of completeness of the transformation represented by it is not definitely known and probably varies widely. Osmond and most others believe that the transformation, while generally far advanced, yet falls materially short of completion; but Benedicks and Arnold (9) believe that it is complete. The former belief that it is a definite phase, e. g., a solid solution of carbon or an iron carbide in either β or γ iron, is abandoned. Its carbon content like that of austenite and martensite varies widely.

Occurrence: It arises either on reheating hardened (e. g., martensitic steel) to slightly below 400°, or on cooling through the transformation range at an intermediate rate, e. g., in small pieces of steel when quenched in oil, or quenched in water from the middle of the transformation range, or in the middle of larger pieces quenched in water from above the transformation range. With slightly farther reheating it changes into sorbite; with higher heating into sorbitic pearlite, then slowly into granular pearlite, and probably indirectly into lamellar pearlite. It occurs in irregular, fine-granular or almost amorphous areas, colored darker by the common etching reagents than the martensite or sorbite accompanying it. A further

common means of distinguishing it from sorbite is that it is habitually associated with martensite, whereas sorbite is habitually associated with pearlite.

Areas near the boundary between troostite and sorbite are sometimes called troosto-sorbite.

Properties: Hardness, intermediate between that of the martensitic and the pearlitic state corresponding to the carbon content of the specimen. In general the hardness increases, the elastic limit rises, and the ductility decreases, as the carbon content increases. Its ductility is increased rapidly and its hardness and elastic limit lowered rapidly by further tempering, which affects it much more markedly than sorbite.

Sorbite (Fr. Sorbite, Ger. Sorbit). Aggregate. (Arnold, sorbitic pearlite.)

Definition: In the transformation of austenite, the stage following troostite and osmondite, if this stage is recognized, and preceding pearlite.

Construction and Composition: Most writers believe that it is essentially an uncoagulated conglomerate of irresoluble pearlite with ferrite in hypo- and cementite in hyper-eutectoid steels respectively, but that it often contains some incompletely transformed matter.

Occurrence: The transformation can be brought to the sorbitic stage (1) by reheating hardened steel to a little above 400°, but not to 700°, at which temperature it coagulates into granular pearlite; (2) by quenching small pieces of steel in oil or molten lead or even by air-cooling them; (3) by quenching in water from just above the bottom of the transformation range, Ar_1. Sorbite is ill-defined, almost amorphous, and is colored lighter than troostite but darker than pearlite by the usual etching reagents. It differs further from troostite in being softer for given carbon content, and usually in being associated with pearlite instead of martensite, and from pearlite in being irresoluble into separate particles of ferrite and cementite.

As sorbite is essentially a mode of aggregation it cannot properly be represented on the equilibrium diagram. Its components at all times tend to coagulate into pearlite, yet it remains in its uncoagulated state at all temperatures below 400°.

Properties: Though slightly less ductile than pearlitic steel for given carbon content, its tenacity and elastic limit are so high that a higher combination of these three properties can be had in sorbitic than in pearlitic steels by selecting a carbon content slightly lower than would be used for a pearlitic steel. Hence the use of sorbitic steels, e. g., first hardened and then annealed cautiously, for structural purposes needing the best quality.

Manganese Sulphide (Fr. Sulphure de Manganèse, Ger. Schwefelmangan), MnS (Arnold and Waterhouse). Metaral.

Occurrence, etc.: Sulphur combines with the manganese present in preference to the iron, forming pale dove or slate gray masses, rounded in castings, elongated in forgings.

Ferrous Sulphide (Fr. Sulphure de Fer, Ger. Schwefeleisen), FeS. Metaral.

Occurrence: The sulphur not taken up by the manganese forms ferrous sulphide, FeS, which, probably associated in part with iron as an Fe—FeS eutectic, forms by preference more or less continuous membranes surrounding the grains of pearlite. Color, yellow, or pale brown.

Sulphur Prints: When silk impregnated with mercuric chloride and hydrochloric acid (Heyn's and Bauer's method) or bromide paper moistened with sulphuric acid (Baumann's method) is pressed on polished steel, the position of the sulphur-bearing areas, whether of FeS or MnS, records itself by the local blackening which the evolved H_2S causes. Phosphorus bearing areas also blacken Baumann's bromide paper.

MISCELLANEOUS.

Eutectoid, Saturated, etc.: The iron carbon eutectoid is pearlite. Steel with more carbon than pearlite is called hyper-eutectoid, that with less is called hypo-eutectoid. Arnold's names "saturated," "unsaturated" and "supersaturated," for eutectoid, hypo-eutectoid and hyper-eutectoid steel respectively, have considerable industrial use in English speaking countries, but are avoided by most scientific writers on the ground that they are misleading, because, e. g., there is only one specific temperature, A1, at which eutectoid steel is actually saturated, and, if any other temperature is in mind, that steel is not saturated. Above A1 it is clearly under-saturated.

The objection to the names sorbite, troostite, martensite and austenite, that each of them covers steel of a wide range of carbon content, is to be dismissed because a like objection applies with equal force to every generic name in existence.

In November a Russian cotton congress was held at Tiflis. There were 300 delegates present, including the governors of the four cotton-growing governments in Transcaucasia—Tiflis, Kutais, Erivan, and Yelizavetpol—and representatives of the government and of various societies and organizations. The object of the congress was to discuss methods of improving and extending cotton cultivation in the Caucasus.

The total value of gold bullion and ore exported from Chosen (Korea), during 1911 was $4,648,674. Exports of graphite, nearly all of which went to Japan, amounted to 131,044 tons, valued at $65,885. Only $355 of copper ore was exported during the year. The salt fields at Kwangyang Bay are said to be capable of producing 160,000,000 lbs. per year, and are now under development.

STANDARD MAGNIFICATION FOR MICROGRAPHS.*

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During the last ten years the science of metallography has passed from the realm of theory and the dream of a few scholars, and has become an essential tool of progressive manufacturers and consumers of the various metallic alloys. The service that this science is now rendering is inestimable, and the future advances in the knowledge of the constitution of ferrous and non-ferrous alloys will depend to a great degree upon the information and data obtained by the metallographist.

The career of metallography has been very similar to that of analytical chemistry—first scoffed at by the many, and little understood even by the scientists; then passively tolerated by a few and finally accepted by all as indispensable. Today metallography is an accepted and generally used science, and our knowledge of the art is so far advanced that many await with impatience and eagerly read, consider and digest each new contribution to the data on this subject and accept new and improved apparatus and methods gladly.

To the end that the work of independent investigations may increase in value to the many, the authors wish to attract the attention of all engaged in this work to the advisability of employing standard magnifications.

Our knowledge of the structural transformations of alloys is primarily based on what can be seen with a lens, the first form used being the eye, followed by magnifying glasses and microscopes of various enlarging power. From the image observed, we obtain data upon which our theories are based and strengthened. Obviously, then, in discussing these images with others it is of the utmost importance that we should give to the reader or hearer, as perfectly as possible, a clear reproduction of the observed image. If we attempt to portray the image by verbal description, we quickly discover the limitations of human speech. By photographing the structure under discussion, each person may see the original data himself and be able to follow our discussion and at the same time draw his own deductions and conclusions.

Consequently, practically all the recent articles on the subject of metallic alloys are more or less profusely illustrated with micro-photographs. The micrographs are interesting, and generally are well chosen to illustrate the point at issue. But perhaps we remember seeing a similar structure in another recent article. We turn to it and compare it with the first. Then our troubles begin; for the first picture was taken at a magnification of 475 diameters, while the second was taken at a magnification of 90 diameters. What are we to do? We must try, in our mind's eye, to reduce the one or to enlarge the other. After more or less mental gymnastics, which as a rule leave us little better off than before, we may turn to another illustration of a structure taken at a magnification of 500 diameters and then reduced one-third—more gymnastics!

TABLE OF SOME MAGNIFICATIONS FOUND IN METALLOGRAPHIC LITERATURE.

No.	Author.	Magnification used.
1	Alloys Research Committee	10, 20, 50, 60, 130, 140, 640, 850, 1000
2	Arnold	10, 45, 50, 60, 65, 66, 200, 250, 260, 315, 360, 460, 600, 650, 1000
3	Boynton	100, 250, 500, 750, 1000
4	Beredict	300, 400, 1000
5	Campbell	30, 40, 120, 500
6	Carpenter	150, 1000
7	Charpy	30, 60, 100, 200, 500
8	Guillet	200
9	Hadfield	50, 100, 250, 1000
10	Kroll	143, 150, 220, 250, 400, 509, 540, 600, 650, 840, 870, 900
11	Law	10, 100, 200, 1000, 2000
12	Levy	120, 200, 600, 1650
13	Longmur	155, 1000, 3000
14	Rosenhain	40, 150, 200, 400, 800, 1200, 1800
15	Stead	40, 50, 60, 80, 100, 125, 250, 300, 350, 460
16	Sauveur	100

In looking up the literature on some subject it is not unusual to find a dozen or more different magnifications, which vary in such odd multiples as to make comparison of grain size and structure mass impossible. We have seen subjects illustrated with magnifications not only of slight variation, but of such odd numbers as 75, 80, 90, 125, 130, etc. Of course, all of these do not occur in one man's article, but they often occur in two or three articles dealing with the same subject. The result of such a chaotic state of affairs is a loss in value of the work done by the various writers, to themselves and to others, since the data obtaind by one man are not readily compared with those obtained by the others, and sometimes are not at all comparable.

Every one has met with this unfortunate situation in the course of his work, and, realizing the seat of the difficulty, has limited himself to a few chosen powers in his own micrographs. The chosen powers of one man, however, may be and often are different from those chosen by another man, so that the condition of affairs, though improved, is not yet satisfactory.

We have carefully looked through the literature of numerous subjects and have studied the works of many metallurgists, and herefrom have prepared a table which will show the magnifications various authors have used in their work.

*Paper presented at the 6th Congress of the International Association for Testing Materials.

†Halcomb Steel Co., Syracuse, N. Y.

A study of this table indicates the chaotic state which exists. In the past, microphotographs have been looked upon more as pictures, and with little regard for the magnification. That this is true may be seen in the liberties taken by publishers in reducing the picture to fit the convenience of the page. Very often the amount the picture is reduced is not even mentioned. Considering the conditions that prevail in other lines of work (in tensile testing we have a prescribed test piece; in chemical work we express our results in parts per hundred, etc), why should we continue to express our metallographic results (which are difficult to interpret under the best conditions) in any magnification from 1.0 up, according to the dictate of the convenience of the apparatus and the operator?

Another point of interest in published micrographs is the truth of the reproduction. Some are printed on smooth, glossy paper, where the detail is expressed clearly; others are printed on the rough ppaer of the ordinary printed page, where all delicate detail is lost and the whole picture becomes of an impressionistic nature. It is necessary that the detail of the micrograph be absolutely expressed if the pictures are to be of any value to others. It therefore behooves those interested to formulate some plan of reproduction for publication purposes which will improve the value of the picture and the amount of detail expressed.

The question that presents itself is naturally: How shall we choose our standard magnifications, and what shall they be? The first part is easily answered. Appoint a committee of competent men, just as we do in other testing work, and let them receive suggestions from metallographists in general, and then let them draw up a set of standard magnifications. The second part is a little more difficult, and the authors do not feel prepared to recommend any particular set of standards. The following are a few suggestions that may, however, be of interest:

The standard chosen should be as near as possible to those magnifications obtained with the ordinary combinations of objectives and eyepieces furnished by the various makers of instruments, so that a specimen may be studied readily in comparison wtih a micrograph of another specimen.

The standards should vary as uniformly from 1.0 up as is possible in conformity with the first condition.

The standards should be as few in number as possible, so that all work of the same character may fall into the same group.

The standards should be sufficiently numerous (a) to allow both general views of a specimen, and details of parts of the general view when necessary; (b) to allow the structure to be shown at best advantage, since any given structure is genrally best seen within a certain range of magnifications.

The above considerations are only the few that have happened to occur to the authors, and are given with the hope of stimulating discussion and criticism which may result in a satisfactory set of standard magnifications for micrographs.

MANUFACTURE OF SOFT STEEL TUBES IN RELATION TO CORROSION.*

By F. N. SPELLER.

Before discussing the influence of manufacture on corrosion it may be well to touch briefly on certain theories of corrosion and adopt that one which best explains the phenomena observed. For this purpose we may confine our attention to what has been called the "carbonic acid" and the "electrolytic" theory. Since it has been proved by Whitney, Cushman, Walker and others, that iron is slightly soluble in very pure water, we need not argue whether this is due to the presence of a few molecules of carbonic acid or whether in absolutely pure water the iron would have been insoluble, both propositions being extremely difficult to prove experimentally. It will suffice to explain the known facts regarding this initial reaction of corrosion by a broad application of the electrolytic theory on the basis that the purest water known contains hydrogen ions and has the power to dissolve nearly anything with which it comes into contact, including iron. Following the solution of iron, which in itself is so slight as to be of no practical concern, we find some very important reactions, all of which have to do with continuous corrosion and which if not checked cause great damage. The cyclical effect of carbonic acid, the oxidations and precipitation of iron as ferric hydroxide, and the depolarization caused by the combination of oxygen in solution with the hydrogen set free during the solution of iron, are the main secondary reactions, particularly the two last.

When the electrolytic theory was first generally discussed several years ago, some of its prominent advocates laid special stress on the "attack by hydrogen ions" and insisted that by greatly increasing the concentration of hydrogen ions a comparison of the relative durability of various irons under corrosion would probably be determined in an hour or so. This became generally known as the "acid test," the use of which, in the light of experiment and experience, was properly discouraged.

Committee A5 (on corrosion) of the American Society for Testing Materials, in their annual report (Proc. A. S. T. M., 1909, p. 300) concluded that "the results so far obtained show that this test is not generally applicable and in some cases may be very misleading."

There is a great deal of work bearing on this matter, but some tests made by the Bureau of Steam Engineering, U. S. Navy Department, and the Research Laboratory of the National Tube Company, serve to illustrate the inconsistency found between tests made in aerated water and in 20 per cent sulphuric acid. (See Table 1 and 1a.)

For some purposes where acid waters must be dealt with or where the air is excessively laden with sulphurous acid from coal, acid-resisting steels doubtless

*From the Journal of the Society of Chemical Industry.

have a useful field, but even here the metals should not be compared by a quick test made in strong acid, as the damage may be different when the combined reactions are met with in service.

The purer the iron is made, the more resistant it becomes to acids. A very highly refined open-hearth steel (ingot iron) is made with this in view. The addition of 0.1 per cent of phosphorus as found in soft Bessemer steel renders the metal much more soluble, but if to the same iron about 0.1 per cent copper is added, the solubility in acid is reduced to that of low phosphorus steel and by increasing the copper to 0.35 per cent the solubility of Bessemer steel under the same acid test is less than highly refined iron, and the same amount of copper in soft open-hearth steel low in phosphorus is still more marked. (See Table II for a comparison of various grades of these materials.)

Natural corrosion, however, as has been shown by tests in the atmosphere, in water, and in pipes buried in the ground, has about the same effect on commercial iron and steel made with equal care, regardless of the composition or method of manufacture.[1] In fact, there is good practical evidence in tests now in progress which indicates that Bessemer steel well made is better in this respect than the purer commercial irons, provided, of course, the environment is not decidedly acid. The same seems to be true of the newer copper-steels, which, however, have not yet been in service sufficiently long to determine their value under natural corrosion. There is this to be said, however, in favor of the use of a small percentage of copper in soft steels; the quality of the metal can be regulated according to requirements, the strength is slightly increased without loss of ductility, and the copper is readily dissolved by the iron and shows little tendency to segregate. Moreover, the cost is low compared with making extremely pure iron produced in an open-hearth or electric furnace.

If the electrolytic theory be correct, why is there no clear relation between tests made in strong acid and those under corrosion? Two explanations suggest themselves. First, the impurities and irregularities which occur on the surface of commercial iron and steel, such as mill scale, rust, carbon deposits from the atmosphere, etc., have a much greater difference of potential with the metal than is usually found between adjacent points on the clean surface of the metal. This explains the local corrosion known as pitting, which is apparently equally liable to occur in the purest or crudest of commercially rolled iron or steel, provided the latter is uniform enough to pass the ordinary qualifications as regards quality. Or, in the second place, considering that in nearly all natural corrosion a large excess of oxygen is present in solution (the internal corrosion of hot water piping is a good example), it seems remarkable that the different rates of solubility do not have free sway and cause the less soluble iron to corrode at a proportionately slower rate. This is, as we have shown, not according to observed facts, and suggests that possibly the speed of the secondary oxygen reactions is not rapid enough to keep up with the solution of even the slower dissolving irons, so that (within the limits) the relative rate of solution of irons in water is not a determining factor.

Considering, then, the influence of manufacture on corrosion, it must not be inferred that the composition and method of manufacture of the steel are immaterial. On the other hand, the question of uniformity in chemical composition and physical properties between different points on the surface must be carefully looked to, this, we believe, being much more important as a rule than the composition of the metal. The best made iron or steel will corrode unevenly when outside forces are allowed to exert their predominating influence, as is usually the case in service when no preventative measures are taken. Nor should it be assumed, because the ordinary elements usually present in steel are low, that such metal is less liable to be irregular, for under such conditions the iron is particularly sensitive to oxygen and absorbs this, probably the most injurious of all elements, under certain conditions of heating, much more readily than would a less pure steel made by the same process.

The influence of composition in soft steel may be referred to under the commonly occurring foreign elements.

Carbon, owing to the various forms it takes in steel, has a variety of effects on corrosion which are not as well understood as could be wished. The small amount present in soft steel probably has little influence one way or the other.

Manganese has been held responsible for more unexplainable failures than perhaps any other element, but, as a matter of fact, it is one of the easiest of all foreign elements for the iron to take up; there being very little segregation, and with reasonable precautions a homogeneous mixture is easy to obtain. Moreover, according to recent researches most of the manganese compounds are either neutral or electro-positive to iron.[2] According to the investigations of Prof. W. H. Walker,[3] Ira H. Woolson,[4] Henry M. Howe,[5] and others, based on many comparisons of wrought iron pipes (practically free from manganese) with soft steel (carrying 0.3 per cent to 0.4 per cent manganese) under the same conditions, no difference in quality or general character of the corrosion could be found.[6]

Phosphorus does not appear to be objectionable as regards natural corrosion; in fact, there seems to be reason for believing that it protects the iron to some extent. Careful experiments by Diegel[7] and our experience of many years with Bessemer and open-hearth steel tubing seem to support this view.

Sulphur in amounts over 0.06 per cent is undesirable, but modern methods control the amount of sul-

[1] See foot-note references [2], [3], [4], [5], [6], [7] and [8].

phur within narrow limits and it will rarely exceed this amount in American steels, the general average being much lower.

Nickel in the usual proportion used (3.5) protects the iron and increases its resistance to corrosion about 20 per cent.

Oxides and cinder, whether included in the metal or on the surface, are objectionable, being more strongly electro-negative than other foreign matter. It is one of the most important points having to do with general quality and durability and requires more vigilance to control the lower the carbon content of the iron. The use of a large mixer, means for controlling the temperature of the bath in refining, and fine crushing of the ferromanganese are obvious necessities. The steel should be poured into the ladle as cold as possible and should exhibit a thorough reaction with the additions in the ladle, after which three or four minutes should be allowed for the blanket of slag to take up the oxidized products before teeming into moulds. The uniformity of the steel may be easily checked by comparing the analyses of tests taken from the first ingot with the last few pounds of steel out of the ladle. Such check analyses are made regularly where a specially homogeneous metal is desired.

Physical irregularities are just as much to be avoided as are chemical variations and require intelligent heat treatment of the metal and sufficient work. Steel which is spongey or honeycombed requires several times as much work to reach its maximum strength as steel which is solid in the ingot.[8]

COMPARISONS OF CORROSION OF BOILER TUBE MATERIALS IN AERATED WATER AND ACID.

Samples were first immersed in aerated water at normal temperature for 64 weeks; test pieces 2″x½″x 1/16″ were cleaned thoroughly and placed in a 20 per cent solution of sulphuric acid for one hour. Loss is shown in grams per square inch under test.

Following is a summary of tests, Table II, on various materials made by submerging in 25 per cent (by weight) sulphuric acid for three hours. The pieces were 2″x1.2″x1.8″ cut from 2-in. pipe. Temperature at start, 35° C.

TABLE II.—ACCELERATED CORROSION TESTS.

	Average loss. Grms. per sq. in. of surface.
Regular Bessemer pipe steel	0.6120
0.35% copper Bessemer pipe steel	0.0088
1.00% copper Bessemer pipe steel	0.0035
Regular open-hearth pipe steel	0.2112
0.20% copper hearth pipe steel	0.0061
3.25% copper hearth tube steel	0.0148
Ingot iron	0.0138
0.40% copper open-hearth pipe steel	0.0038
1.00% copper open-hearth pipe steel	0.0023

TABLE I.

	Loss in aerated water.	Loss of same piece in 20 per cent sulphuric acid.	Test piece showing:	
Lap Weld Bessemer Steel.				
Least	1.479	0.1307	Least loss in 20 per cent acid gave	0.1249
Greatest	2.031	0.1290	Greatest loss in 20 per cent acid	0.1388
Average of 23 pieces	1.729	0.1322		
Cold Draw Seamless, Open-hearth Steel.				
Least	1.512	0.0423		
Greatest	2.262	0.0379	Least loss in 20 per cent acid	0.0308
Average of 21 pieces	1.926	0.0354	Greatest loss in 20 per cent acid	0.0439
Lap Weld Charcoal Iron.				
Least	1.540	0.1116		
Greatest	1.988	0.1009	Least loss in 20 per cent acid	0.0960
Average of 22 pieces	1.753	0.1098	Greatest loss in 20 per cent acid	0.1250
Hot Drawn Seamless, Open-hearth Steel.				
Least	1.384	0.0354		
Greatest	1.881	0.0362	Least loss in 20 per cent acid	0.0279
Average of 24 pieces	1.662	0.0330	Greatest loss in 20 per cent acid	0.0376

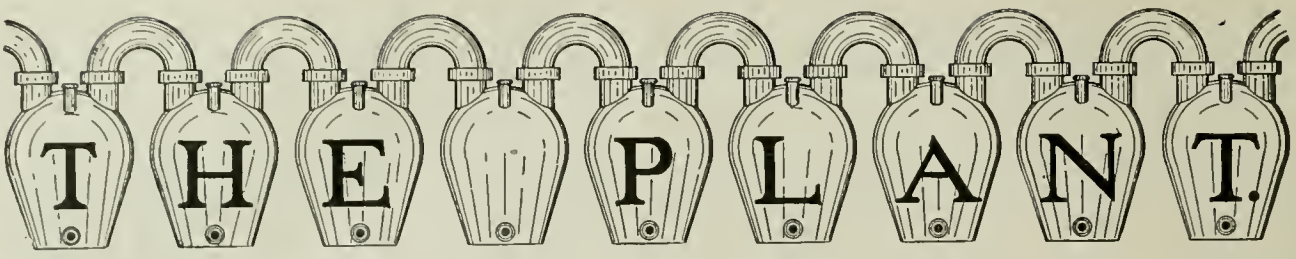
TABLE I[9].—SUMMARY.—AVERAGE RESULTS OF CORROSION IN GRAMS PER SQUARE INCH.

	Series I.		Series II.	
	In aerated water 64 wks.	In 20 per cent acid on smooth pcs.	In aerated water 61 wks.	In 20 per cent acid on pitted pcs.
Charcoal iron	1.752	0.1098	1.772	0.0823
Bessemer steel 0.07 carbon	1.729	0.1322	1.734	0.0897
Cold drawn seamless steel Bessemer	1.926	0.0354	1.871	0.0121
Hot drawn seamless steel open-hearth steel, 0.15% carbon	1.652	0.0330	1.759	0.0120

Note.—Series I was made on test pieces machined and ground to size as in Table I. Series II includes tests made on samples cut from sections of tubes after exposure in aerated water without grinding down the pitted or corroded surface, as was done in Series I.

A committee of manganese producers of southern Russia has requested permission to call a congress of manganese producers to discuss various questions of interest to the industry. Sanitary measures for the protection of mine employes; insurance of workmen; hospital funds; bringing water to the mines; construction of branch railway lines in mining regions; construction of elevators at Batum for loading ore; transportation problems, and statistics of mine production, are among the subjects to be considered.

[8] J. W. Cobb, Jour. Iron and Steel Institute, Vol. 1 (1911).
[9] Journal of Engineering and Industrial Chemistry, Amer. Chem. Soc. (1912).
[4] Engineering News (Dec. 3, 1910).
[5] Proceedings Am. Soc. for Testing Materials (1908).
[6] J. N. Friend, "Corrosion of Iron" (1911), p. 269.
[7] Diegel, "Verhandlungen des Vereins zur Beförderung des Gewerbefleisses" (1903), 5, 157.
[8] Report on Tests of Metals, United States Watertown Arsenal (1909).



NONINFLAMMABLE CELLULOID COMPOUNDS.*

Nearly four-score years have elapsed since an ester of a carbohydrate was first prepared, Braconnot having announced in 1833 the existence of a body obtainable by the action of concentrated nitric acid upon starch, and called by him "xyloidine." Subsequently Liebeg, Payen, Pelouze, Gladstone, Bechamp and Bouijs-Ballot investigated more completely the chemical and ballistic properties of "explosive starch meal," "nitramidine," "pyroxam," or "pyramidon"—names at that time embracing the various products obtained by the nitration of commercial starch. Schönbein in 1845 or 1846 succeeded in nitrating fibrous cellulose (cotton), and made the (then fanciful) prediction that his "explosive cotton wool" would soon entirely supersede gunpowder in warfare—a prediction that is rapidly being realized.

The investigations on acetylation communicated by Paul Schützenberger in 1862 were followed three and eight years later by the presentation of *Memoirs* to the French Academy upon the acetation of carbohydrates, in which is described the acetation of fibrous or normal cellulose. While it is evident that the products obtained by Schützenberger showed serious degradation of the cellulose molecule coincident with acetylation, yet it nevertheless must be admitted that he thereby laid the foundation for the non-explosive and relatively non-inflammable esters of cellulose, as direct commercial competitors for the longer known inflammable nitrates. Girard, Liebermann, Franchimont, Vignon, Skraup, Cross and Bevan, Ost, Schwalbe, Eichengrün, and others, have elaborated the mechanics of the acetylation process, and investigated the intimate relations of hydrocellulose formation in the presence of esterifying agents.

The first patent for an acetylated derivative of cellulose was granted to Cross and Bevan in 1894, since which time the art has ramified to a large number of industries, as attested by the nearly nine hundred patents the writer has collected, and which have been issued in the past eighteen years on this subject. From the first a serious drawback to advancement has been the cost of materials for production. Acetylchloride was soon discarded on account of the cost, but the necessity for the presence of both glacial acetic acid and acetic anhydride in the acetylizing mixture, has never brought the cost of the finished product to a point where it could successfully compete in price with the cellulose nitrates. Although the price of acetic anhydride has been materially reduced in the past few years, the cost of the production of cellulose acetates has still been in excess of that of the nitrates.

This fact undoubtedly influenced investigators in their search for other esters which, while at the same time noninflammable and nonexplosive, could still be produced at a figure admitting of direct commercial competition with nitrocellulose. The propionates, butyrates, acetonitrates, and mixed esters of the acetic acid group, all required the use of relatively large amounts of the anhydride corresponding to the ester produced, and which was the most expensive constituent in the esterizing mixture. The least expensive anhydride in comparison to the corresponding acid which is applicable is perhaps acetic anhydride, which is at present about twice as costly as acetic acid.

However, about ten years ago formic acid began to be produced in large quantities and at a (then considered) reasonable cost, and it is significant that coincident with the appearance of large quantities of concentrated formic acid as a commercial commodity, the industrial possibilities of formylated cellulose began to receive the serious attention of chemists. The fact that in the formylation of cellulose, no counterpart of acetic anhydride—the most expensive constituent of the acetating mixture—is required in their preparation, is, in the writer's judgment, the principal factor in the great activity displayed in this field at the present time. It appears quite probable that in the near future the cellulose formates may be produced in unlimited amounts commercially, at a cost at least not in advance of the present cost of nitrocellulose, starting with the same source of cellulose.

The cellulose formates may be prepared by many of the methods applicable to acetic ester formation, and from hydrocellulose or other modified cellulose without resort to esterifying agents, cellulose hydrate and especially the waste from artificial silk manufacture. Denitrated nitrocellulose filaments and viscose silk waste have been found especially suitable. As with the corresponding acetates, much time and experimentation has been devoted to the selection of suitable hydrolyzing agents, and the conditions under which they yield most dependable results. For the formylation of natural cellulose (cotton), the most important advocated have ben sulphuric acid, zinc chloride and sulphuric acid, gaseous hydrochloric acid, the halogens, combination of hydrochloric and sulphuric acids in the form of sulphuryl chloride, pyrosulphuryl chloride, and chlorosulphonic acids. Ethyl sulphuric

*From a paper read before the Society of Chemical Industry by Edward C. Worden, Ph. C., M. A.

acid may also be included. The cellulose, if desired, may be dyed before formylation. The phospho-formates of the Vereinigte Glanzstoff Fabriken are claimed to be especially valuable when combined with certain plastic-inducing bodies as triphenyl phosphate.

Berl and Smith have shown that cellulose monoformate may be prepared by the action of substantially absolute formic acid in the presence of five per cent by weight of sulphuric acid, but they were unable to obtain technically useful esters. Woodbridge found that when formic acid of specific gravity 1.20 is substituted for the anhydrous compound no formate results, while on the other hand, where the most concentrated acid is employed, filter paper dried at 100° C. is as efficient a starting material as the cellulose prepared according to the method of Girard. In his preferred method 18 Gm. of dried filter paper is treated with 100 Gm. of formic acid of specific gravity of 1.22 and 10 Gm. sulphuric acid, the whole being kept at 30 to 35° C. for 16 hours. After thinning with more formic acid and filtration of the viscous mass from unconverted cellulose, the mixture was precipitated in a large bulk of water, washed to neutralization and dried at a low temperature. The product thus obtained was found to be soluble in formic acid or zinc chloride, insoluble in methyl, ethyl, or amyl alcohols, acetone, chloroform, carbon tetrachloride, ethyl acetate, amyl acetate, aniline, or dilute sulphuric, nitric, or hydrochloric acids. The insolubility of the formic ester in acetylene tetrachloride is a qualitative distinction and separation from cellulose acetate. Saponification yielded 23.1 per cent of formic acid, the monoformate requiring 24.2 per cent.

The recuperation of formic acid from a mixture with sulphuric or other mineral acid, presents difficulties, and the solution of the cellulose is subjected to sufficiently speedy decomposition owing to the presence of the comparatively large amounts of energetic mineral acid. Where the ultimate product is required to possess the maximum strength, as when the material is used for artificial silk filaments or continuous film formation, these objections have weight. The Nitritfabrik Akt. Ges. have devised a process for rendering cellulose soluble in formic acid in order to obtain formylated cellulose solutions applicable for spinning, by first forming hydrocellulose, washing free from inorganic acid and drying, when the dry product may be directly formylated by solution in formic acid and zinc chloride, with the elimination, the patentees claim, of the decomposition phenomena referred to above.

Deming prefers dry hydrochloric acid gas, his method being to saturate 3 Gm. of filter paper in 100 Cc. of formic acid which has been previously saturated at room temperature with dry hydrochloric acid. The product after four hours is precipitated, and found to be slowly soluble in formic acid, slightly soluble in pyridine, and insoluble in the other reagents which dissolve the cellulose acetates. If allowed to remain in the acid liquid twenty-four hours before precipitation, the ester first formed is partially saponified to a modified cellulose. Instead of hydrochloric acid, the halogens themselves have been found suitable in the hands of the Actien-Gesellschaft für Anilin Fabr., chloride, bromine, or iodine monochloride, iodine trichloride, iodine monobromide, or bromine chloride being specified.

According to the patented process of the J. P. Bemberg Aktiengesellschaft, gaseous hydrochloric acid gas is preferable because the process takes a more regular course and less secondary products are formed, the method being to introduce 2 to 4 parts of dry hydrochloric acid into 100 parts of 98 to 100 per cent formic acid, after which 20 to 30 parts of dry cellulose is gradually added to the mixture. After the lapse of several hours, assisted by repeated stirring, the cellulose passes substantially into solution, the temperature being kept between 15° and 18° C. meanwhile. At the completion of the formylating process the mass is precipitated in a large bulk of water, washed until neutral and air dried. Thus prepared, the formylcellulose forms a white powder soluble in formic acid, zinc chloride solution, and partially in dilute acetic, hydrochloric and sulphuric acids.

The energetic action of sulphuric or hydrochloric acids may be considerably modified without materially decreasing its efficiency by combining the two, sulphuryl chloride with or without zinc chloride being used. In the latter method, chlorides of sulphuric acid such as $SO_2OH.Cl$, SO_2Cl_2, and $S_2O_5Cl_2$ are employed, as indicated in the following example. One hundred parts by weight of cellulose—preferably previously rapidly dried artificially at 105°—are soaked with 500 parts or more of formic acid of 98 to 100 per cent strength and 20 to 30 parts of sulphuryl chloride, solution being complete in one or two days. Where zinc chloride is used, either sulphuryl chloride or chlorosulphonic acid is specified in addition to formic acid. The white voluminous product obtained by precipitation of the formylated mass in a large volume of water is soluble in formic acid and in zinc chloride solution, and is distinguished from the formylcellulose of the older art by being soluble in pyridine. The patentees state that upon evaporation of a solution of formylcellulose prepared in the above described manner, a translucent, flexible film remains.

In the method Dreyfus cellulose esters may be produced even in the cold by the action of formic acid on cellulose or its derivatives in the presence of a small quantity of an aliphatic or aromatic ester of sulphuric acid, as ethyl-sulphuric acid. Where the reaction is carried on in the absence of solvents, gelatinous products are obtained, whereas in the presence of solvents, viscous products result.

The Vereinigte Glanzstoff Fabriken have shown that the cellulose hydrates, which may be obtained in large quantities and at a low price in a form, for example, of denitrated nitrocellulose threads, lustracellu-

lose filaments (cuprammonium process), or viscose, as refuse from the cellulose, artificial silk industry, are highly adapted for serving as raw material for formylcellulose manufacture. They merely introduce the refuse material into formic acid of 95 to 100 per cent strength, and warm the mass gently until the cellulose passes into solution, when the fluid may be directly utilized by forcing through spinnerets into artificial filaments. The solution of the waste may be effected at the ordinary temperature, is accelerated by warming to 40 to 50 C., while at still higher temperatures formylation proceeds more rapidly with the formation of thinly viscous solutions of impaired strength, due probably to further hydrolysis of the cellulose hydrates and the formation of more highly and complexly hydrated formylcelluloses. The best criterion of the product which it is desired to obtain is the gloss, transparency and elasticity of the films prepared from the solutions.

If desired, the cellulose may be dyed before formylation, thus producing various shades, the algol, indanthrene, rosanthrene, helindon, katigen, immedial and similar classes of dyestuffs being stable against the acid agents employed in the formylating process. For example, 200 parts of cotton dyed with indanthrene are formylized with 100 parts of formic acid and 3 to 10 parts of sulphuric acid, a dark blue solution being obtained from which the deep blue formylcellulose can be precipitated out and washed in the usual manner with water without detriment to the color. It is soluble in the usual solvents, and blue films may be produced from the solutions. The process may be carried out in an analogous manner by the use of other suitable dyestuffs.

A careful survey of the historical development of the cellulose nitrates will show that the broadening of their technical utilization has occurred simultaneously with the discovery of new solvents, or the adaptation of known solvents to new uses. It was lack of suitable solvents which hindered Parkes, Spill, Barnwell and Rollason, Mennons, Cutting, Pierson, McClelland, Kendall and Trested in the development of the nitrocellulose art, and the appreciation of the value of the solvent over the nitrocellulose that laid the basis of success of the thermoplastic cellulose nitrates typified by celluloid. An analogous condition is being found at the present time in attempts to perfect the cellulose acetate industry. Energy is being focussed on the discovery of suitable liquid and solid solvents, bodies which, like camphor, are thermoplastic and relatively nonhygroscopic. In this direction the cellulose ester art is at a standstill awaiting the advent of a solvent which will have the desirable properties imparted to the cellulose nitrates by camphor. Resorcinol diacetate, benzophenone, acetated castor oil, acetin, camphor, thymol, chloral hydrate, are solid or semi-solid bodies which have been proposed for this purpose, but their defects are many.

The liquid solvents for cellulose acetate, such as acetylene tetrachloride alone or with methyl alcohol, triphenyl phosphate in solution, benzyl benzoate, methyl formate, chloroform, acetone, chloral, chloranisol, chlorhydrins, chlorobenzyl alcohol, creosote, diacetone alcohol, epichlorhydrin, mannol, naphthyl acetate, nitrobenzene, nitromethane, pentachlorethane and alcohol, benzyldihydropulegone, chloral alcoholate, acetyl alkyl aniline, naphthol acetate, chlorpalmitic acid, ethylenechlorhydrin, acetodichlorhydrin and alcohol, ethylene chloride and alcohol, ethyleneacetochlorhydrin, are unsuitable solvents or gelatinizing agents for the cellulose formates. The utilization of the formylated celluloses, therefore, is inhibited by too few solvents, or solvents whose field of usefulness is too narrow. It was with the hope to increase the number of useful solvents for formylated cellulose that the descriptive and experimental work outlined in the latter portion of this paper was undertaken. If the known solvents and plastic-inducing bodies suitable for the cellulose acetates were equally applicable to the corresponding formates, the technical field for the latter esters would be materially widened.

The vereinigte Glanzstoff Fabriken have found lactic acid to be an excellent solvent for formylated cellulose, Waite having previously discovered the action of this acid on the corresponding acetates. The Vereinigte dissolve 10 parts of artificial silk waste in about 100 parts of formic acid, then add about 50 parts by weight of 80 per cent lactic acid, the excess of formic acid being recovered by distillation in a partial vacuum at a temperature not exceeding 40° C., and recovered for reuse. The viscuous syrup which remains may be drawn into threads, or allowed to solidify into a flexible, transparent mass. If it is desired to remove the acid reaction, dialysis with water is resorted to. It is self-evident that inasmuch as cellulose dissolves in formic acid to form a formylated derivative, the latter after purification is soluble in formic acid. The Internationale Celluloseester Gesellschaft have patented a similar process in which formylated cellulose is rendered plastic by the combined action of formic and lactic acids. Instead of lactic acid, use may be made of phosphoric acid, the commercial syrupy orthophosphoric acid having proved most suitable. Best results are said to be obtained by mixing 1 kilo of approximately 99 per cent formic acid with 1 kilo of commercial phosphoric acid of about 84 per cent strength and 200 Gm. of degreased, slightly bleached cotton stirred in. After remaining for a few hours, the cellulose is converted into a slightly colored viscous solution, which can be worked into fibers, threads and films. In order to make this product plastic a solution of the cellulose formate or cellulose phosphoformate in formic acid is diluted with amyl acetate, amyl formate, methyl alcohol, ethyl alcohol, or a mixture of hydrocarbon and alcohol, the ester immediately separating as a voluminous but coherent mass which falls to the bottom

of the vessel. The supernatant liquid may now be withdrawn, the precipitate washed, there finally remaining a semi-solid, gelatinous coagulum, which is transparent and readily miscible with triphenyl phosphate to a hard, solid, plastic mass. Ellis has described combinations of formylated cellulose with chloral, castor oil, amyl lactate and methyl acetone as being commercially valuable.

George W. Miles, in his patented processes for the partial hydration of acetylated cellulose, greatly extended the usefulness of the cellulose acetates by the observation that in the acetylation process leading to the formation of substantially normal cellulose triacetates, if water be added to the acetylizing mixture—or materials which would induce hydration—the acetated cellulose after a time lost its solubility in chloroform and arrived at that stage of hydration represented by incipient solubility in warm chloroform, at which time it would be found soluble in acetone of 99 per cent or better, and at the same time be found soluble in a large number of fluids in which the normal acetated cellulose will not dissolve. It is the attempt to apply this same principle to the cellulose formates, which form the subject-matter of the experimental portion of this paper, and although the results were negative in character, they are recorded in detail in possible assistance to others.

PREPARATION OF FORMYLATED CELLULOSE.

A grass bleached tissue paper was converted into hydrocellulose by the method of Girard after extraction with hydrochloric and hydrofluoric acids to remove small amounts of iron and silica, the final ash being 0.0016 per cent. Thus prepared it was a white, rather soft, somewhat friable mass, which, when extracted with boiling water, yielded no water-soluble residue. In the last series of experiments a denitrated nitrocellulose was used, being prepared by the nitration of the same grade of filter paper by a nitrating mixture containing 21 per cent of nitric acid and 63 per cent of sulphuric acid at a temperature of 42° C., the product being entirely soluble in acetone, ether-alcohol, amyl acetate, ethyl acetate, and in crude wood spirits. Denitration was effected with warm ammonium sulphide solution, the denitrated product giving no color reaction with diphenylamine, and 0.0031 per cent of nitrogen in a nitrometer. Two hundred Gm. portions of modified cellulose were placed in convenient glass receptacles, and one kilo of chemically pure formic acid of 99.1 per cent strength added, both cellulose and acid being at room temperature. The mass was vigorously stirred for about one hour, in order to thoroughly disintegrate the hydrocellulose, in order that the subsequent formylation might occur with maximum uniformity. The hydrocellulose (modified cellulose) had then been broken up to an indistinguishable mass which was in no ways transparent, and without the evolution of appreciable heat. Sixty Gm. of fused zinc chloride, previously powdered and ground to a paste in 100 cubic centimetres of absolute formic acid, was next added, and the mass stirred continuously during a period of four hours, the maximum temperature being 42° C. At the expiration of this period the modified cellulose had become partially transparent, very viscous and heavy and substantially homogeneous. The formylating mass was then left at rest 24 hours, during which time the mass became less viscous and nearly transparent, being of a straw-yellow color. It was filtered in the cold through asbestos in a Gooch crucible to remove translucent pellicles of incompletely dissolved material. A portion precipitated by pouring in a thin stream into a large bulk of water and thoroughly washing to a neutral reaction and freedom from zinc salts gave a practically white, voluminous, amorphous powder without odor or taste, insoluble in water, ethyl alcohol, amyl alcohol, ethyl acetate, amyl acetate, soluble 4 per cent in acetylene tetrachloride at 45° C., readily soluble in formic acid, soluble 18 per cent in pyridine at room temperature, which, however, continued to become opalescent and deposit, even after repeated filtrations through hardened filter paper. The above solubility determinations refer to one Gm. formylated cellulose in 5 Cc. fluid. At room temperature, glycerin dissolved 1.3 per cent, acetin 3.7 per cent, quinoline 4.8 per cent, collodine 3.9 per cent, pentachlorethane 1.1 per cent, tetrachlorethane 5.3 per cent, dichlorethylene 1.1 per cent, and epichlorhydrin 2.2 per cent. From none of these solutions could flexible and tenuous films be obtained. The dissolved portion in each instance had the same formic acid content as the major undissolved portion, thus indicating no selective solvent action. The yield was 126 per cent on the weight of the dried modified cellulose, saponification giving 27.1 per cent formic acid, as against 24.22 per cent for a cellulose monoformate.

A sample of 10 Gm. extracted in a Soxhlet extractor with 99.5 per cent acetone gave a solubility of 10.0 per cent, the major portion of which precipitated upon cooling, and did not produce a flexible or coherent film.

Partial hydration of formylated cellulose.—After clarification of the solution containing formylated cellulose in the reacting mixture, by filtration under pressure, 10 per cent of the weight was withdrawn and precipitated, washed and dried, as above stated. The remaining 90 per cent by weight was divided into nine equal portions by weight, and to each was added varying amounts of water diluted with an equal volume of absolute formic acid added to minimize proneness to precipitation upon the addition of water. The containers were then kept at varying temperatures for different lengths of time, precipitated in water, washed to neutrality and dried. The fractions thus obtained were submitted to solubility determinations, in order to see to what extent the partial hydrolysis (if any) had affected the solubility. In none of the fractions obtained could any physical difference be noted, except, perhaps, those submitted to higher temperatures,

or longer contact with the water, were somewhat softer to the feel.

Table I records the per cent by weight of formylated cellulose which was dissolved in tetrachlorethane, chloroform and acetone, all chemically pure and free from water, when one Gm. of formylated cellulose is rotated for five hours with 5 cubic centimetres of solvent, the material filtered, and a measured portion evaporated to dryness. Usually 5 Gm. of formylcellulose and 25 Cc. of solvent were used. Column I shows the volume of water, which after dilution with an equal volume of concentrated formic acid, was slowly added with much stirring to one-tenth the weight of the formylating mixture of 200 Gm. of modified cellulose, and is equivalent to approximately 20 Gm. of modified cellulose. Five, ten and twenty hours express the time which the containers were heated at 35° C. in a thermostat with the quantities of water stated in Column I.

The results obtained indicate, in general, an increase in solubility with the amount of hydrating water added, and the increase of time of the hydration period. The differences obtained are not sufficiently marked or concordant, in the majority of instances, to admit of profitable deductions.

TABLE I.—PER CENT BY WEIGHT OF FORMYLATED CELLULOSE.
Temperature 35° C.

Water added. Cc.	Sample number.	Tetrachlorethane solubility. 5 hrs. per cent.	10 hrs. per cent.	20 hrs. per cent.	Chloroform solubility. 5 hrs. per cent.	10 hrs. per cent.	20 hrs. per cent.	Acetone solubility. 5 hrs. per cent.	10 hrs. per cent.	20 hrs. per cent.
0	b	3.2	4.1	5.7	2.2	2.1	2.8	1.9	4.4	6.2
2	c	2.8	3.9	6.1	2.0	3.1	2.2	3.9	4.8	5.4
4	d	3.1	3.8	5.8	2.9	3.3	1.9	2.8	4.7	6.2
6	e	5.1	7.2	7.7	4.0	4.2	6.0	3.0	3.8	5.9
8	f	5.1	6.4	7.0	4.2	4.8	5.7	3.5	4.1	5.4
10	g	6.2	6.0	7.4	4.0	4.5	5.5	3.9	4.2	5.3
12	h	7.4	8.9	8.7	5.0	7.7	7.2	4.4	6.0	6.2
14	i	7.7	9.2	9.5	6.8	6.6	7.4	5.3	6.6	6.3
16	j	7.9	7.8	9.2	7.9	10.1	10.4	6.7	8.9	9.7

As a result of the increased demand for Portland cement a movement has been started for the establishment of a factory in Bulawayo, Rhodesia, South Africa, a company having been formed in connection with the enterprise. The promoters have secured rights from the government over an area on the Tuli Road (about 14 miles from town) containing enormous deposits of material said to be suitable for the manufacture of a Portland cement which, it is claimed, exhaustive tests have proved to be equal to the best imported. Application has been made to the town council for a site on which to erect the factory.

A "part-time apprenticeship course" is being instituted in Leeds University in connection with the Bradford Technical College, for combined study and work in textile dyeing. Alternative arrangements are offered. During the past year the dyeing school branch of the university had 143 students, 54 attending day and 89 night classes.

THE ESSENTIALITY OF AUTOGENOUS WELDING OF DIFFERENT KINDS OF STEEL AND IRON AND ITS PRACTICAL APPLICATION.*

By MAX BERMANN.

The essential characteristic of autogenous welding is the uniting of the finest particles of steel surfaces in the molten state by the aid of molten steel of the same composition. The melting of these surfaces, and also of the uniting metal (welding wire) is effected by means of a gas flame of very high temperature, generated by a mixture of combustible gas (hydrogen, acetylene, coal gas, benzine) with oxygen under high pressure.

Apart from the cohesional union of the minute particles of the pure metal at the welded joint, uniform, homogeneous composition of the metal at the joint is a condition precedent to a perfect autogenous weld, so that the metal at the joint has the same strength as the other portions of the welded pieces. In the molten condition the minute particles of the material are under the influence of their own force of attraction; and external pressure is therefore superfluous in autogenous welding. The union of the minute particles at the joint by cohesion is therefore attained with greater ease and security than in solid welding. It is, however, essential that the molten part of the joint surfaces should be prevented from solidifying before it is brought into contact with the molten intermediary steel, since otherwise it would be impossible to form a union by cohesion, this being prevented by the slag and oxides on the solidified surfaces.

Hence, clean metallic contact betwen the molten particles of steel can be prevented by oxidation; and this oxidation may result from the use of a welding flame containing an excess of oxygen, or, again, by the solidification of the molten portions of steel in contact with air. Consequently, the welding flame must not have an oxidizing action: and, this condition being fulfilled, the reduction of the oxidized superficial particles will then be effected by the reducing agents (carbon, manganese, silicon, phosphorus) contained in the steel itself.

*Presented at the 6th Congress of the International Association for Testing Materials.

The second principal condition precedent to perfect autogenous welding: homogeneity of the welded joint, consists in the chemical composition and structure being uniform with those of the other portions of the welded pieces. Equality in the chemical composition of the joint implies that the character of the uniting steel must be identical with that of the steel to be welded, and that the same must not sustain any alteration either during or after welding, that is to say, in cooling. At the present time there is no difficulty in selecting a uniting steel that is identical with the steel to be welded, the spark test furnishing reliable and rapid results. "Identicity of sparking implies identical quality of steel."

Alteration in the chemical character of the joint, or even in the parts adjacent thereto, is mainly to be feared when an acetylene or other illuminating gas flame is being used. Experience shows that, in certain circumstances, these gases decompose with liberation of carbon, which combines chemically with the iron and thus changes the quality of the steel.

In order to prevent change due to cementation, the welding flame should have a non-reducing action, *i. e.*, should preferably contain a slight excess of oxygen. In welding cast iron by the autogenous process, alteration in the chemical composition at the joint is inevitable, even when an inert welding flame is used. In molten cast iron the whole of the contained carbon is in the dissolved condition. The rapid cooling and solidification of the molten iron, in consequence of the heat conductivity of the metal, prevents the separation of the original quantity of graphite; so that the percentage of combined carbon in the metal at the joint is greater than elsewhere in the casting, and the iron is therefore harder.

In order to remedy this defect, the added metal used in welding cast iron by the autogenous process should be a correspondingly softer cast iron, or else steel with a higher carbon content. For the reduction of the oxides it is advantageous in this case to use a powdered flux suitable to the quality of the iron. Equal and uniform character of the joint necessitates continuity and a structure corresponding to that of the other portions of the welded metal.

Continuity means close contiguity of the particles of steel, with freedom from gaps, bubbles and extraneous substances (slag, oxides, etc.). This condition is secured, on the one hand by suitable preparation of the channel of the joint, affording admission to the welding flame and the molten uniting metal; and on the other hand by keeping fluid the just previously treated portion of the weld, so as to enable the slag to rise to the surface and keep the weld clean. In consequence of the rapid cooling, the structure of the steel or cast iron at the weld is crystalline; and therefore must be subjected to mechanical after treatment in order to make it uniform with that of the other portions of the welded pieces; otherwise the joint will be brittle, and may also have a lower tensile strength. If mechanical treatment of the weld be impracticable, it should be rendered ductile by annealing; but in such case the use of an imperfectly kindled charcoal fire must be avoided, since this would entail risk of cementing the steel. In the case of cast iron this danger is, of course, non-existent.

From the foregoing it is clear that autogenous welding is far superior to solid welding, the union of the individual particles of iron by cohesion being ensured by their molten condition. Except as regards structure, the attainment of uniformity of character in the weld presents no difficulty, the procedure being the same as in refining molten steel. The well known means and slag formers are used; and uniformity of character is more easily secured in this case, on account of the small quantities of molten material concerned. Nevertheless, and especially in the case of important machine parts that are subjected to alternating stresses, the general application of autogenous welding is prevented by the fact that, up to the present, there has been no possibility of ascertaining whether the welding is successful or not, unless by breaking the piece.

However, given intelligent, conscientious and perfectly reliable workmen, who understand the nature of the autogenous welding process and have acquired the necessary skill and certainty in the practice of same—on which points we can convince ourselves by examining their trial welds, by breaking tests, microscopical investigation of a section through the joint, etc., the only question remaining is the delicate one of unintentional cementation of the steel. Against this defect we are secured by the spark test. After the weld is finished, the joint and its environment, within the sphere of influence of the entire welding flame, are examined. If it be found that any portion has been rendered unsuitable for the purpose for which the work is intended, in consequence of an absorption of carbon, the piece must be rejected, unless the uniformity of the part under consideration can be restored. The skill of the operator is generally recognized to be the main criterion of reliability in autogenous welding; but so far as I am aware, nothing has been published on the question of what this skill consists in. Our discussion of the question of autogenous welding will throw light upon this point as well.

The skill of the operator is manifested in the preparation of the surfaces for the joint; the production, in each case, of a joint channel of suitable dimensions; the choice of the uniting metal and thickness of the rods of same; in determining the superficial areas to be melted at a time so that they can be covered immediately with the molten uniting metal; in estimating the ratio of gas to oxygen; in selecting the appropriate gauze of nozzle; in the manipulation of the soldering tool and keeping it in proper condition; and also in preventing the formation of cracks, during welding and cooling, by the application of a suitable amount of heat to the endangered parts.

The further development of the process of autogenous welding necessitates the elaboration of a method enabling the molten metal to be cooled down slowly, so as to render subsequent mechanical treatment superfluous.

SUMMARY.

1. The essential characteristic of autogenous welding is the union of the welding surfaces, in the molten state, by means of molten metal of the same composition.

2. The clean metallic contact of the minute particles in the joint is assisted by the reduction of the iron oxides or by dissolving them in the slag. The reduction is effected by the reducing constituents in the steel, the dissolving, however, by the aid of slag formers which, in the form of powdered fluxes, are chiefly used in the case of cast iron.

3. Uniform character of the weld is, moreover, ensured by suitably oxydizing the uniting metal by the aid of the spark test.

4. Having convinced ourselves of the skill and trustworthiness of the operator, it is only necessary in important cases to examine the weld and adjoining parts by means of the spark test, in order to see whether any essential alteration has occurred in consequence of the absorption of carbon from the acetylene flame.

The conclusion arrived at by the author is that the success of the welding process is facilitated by the use of a flame with a slight reducing action and of a welding material the chemical composition of which is as nearly as possible identical with that of the body to be welded. For ascertaining the identity of the materials, he recommends the spark test.

The weld in autogenously welded pieces should have the same character as the piece itself. The uniting metal should be examined by the spark test, which also serves as a check on the quality of the weld in steels, inasmuch as it affords security against alterations due to the absorption of cementing carbon.

The value of the total mineral production of Mexico for the fiscal year ending June 30, 1912, is estimated at $104,491,109, in a recent report issued by the Finance Minister. The production of gold was greater than in any of the preceding five years, the estimated value being $24,246,109. Silver made a gain of $4,357,931 over the preceding year, due largely to the higher price of the metal, although there was a gain of 277,680 ozs. in production. The value of the total silver production for the year was $44,653,003. The value of the output of other metals is estimated as follows: Copper, $13,232,051; lead, $2,999,024; zinc ore, $440,129. The report values the output of petroleum at $7,470,000; iron and steel, $3,486,000; coal and coke, $4,482,000.

COMMERCIAL CASE CARBONIZING OF STEEL.*

A paper by Marcus T. Lothrop, Canton, Ohio, read before the American Society of Mechanical Engineers at the recent meeting, contains much valuable information on case carbonizing, based upon a series of exhaustive experiments. In introducing the results of his work, Mr. Lothrop explained that case carbonizing requires that the carbon content of the material on the surface be increased while the original composition of the material in the interior is retained. The operation requires that the user, in a sense, make his own steel and the details of the operation must be understood to the end that the operation may be conducted with the minimum cost and with the maximum certainty and that variations and irregularities shall not creep into the product.

The investigations indicate that, commercially, the case carbonizing operation can be performed in such a manner that the final result will be absolutely uniform and that the advantages which accrue represent the most efficient manner of obtaining the desired physical properties in many constructions. It was with the object of pointing out the causes of and the results effected by irregularity and the means and precautions which must be employed to produce uniformity, that these researches were undertaken.

THE EFFECT OF HEAT TREATMENT.

The first of the experiments was made in order to determine the effect of heat treatment in case carbonizing. The materials used ran from 0.15 per cent. to 0.25 per cent. carbon, basic open hearth: 0.10 per cent. to 0.31 per cent., Halcomb electric furnace nickel steel: 0.20 per cent. and 0.49 per cent., Halcomb electric furnace chrome-vanadium steel, and 0.50 per cent., Halcomb electric furnace chrome-nickel steel. The conclusions from these tests follow: Strength and toughness decrease with increasing depth of case. This is important commercially, for with a certain steel and a certain heat treatment uniformity of strength and toughness is impossible if the depth of case varies.

The critical depth of case at which maximum brittleness and minimum strength occur depends upon the initial carbon content of the steel which is case carbonized. The higher the original content, the smaller the ratio of depth of case to diameter of core at the point where this brittleness occurs. The commercial importance of this point is that the manufacturer using the steel for case carbonizing should know its composition and should vary the depth of the carbonizing effect as demanded by the composition of the metal being used.

Strength and toughness increase with double heat treatment. This result is to be expected, for the dual nature of case carbonized steel requires two thermal treatments properly to refine the composite metal. Strength and toughness increase when the temper is

*From the Iron Age.

drawn at 380 degrees Fahrenheit. This operation does not decrease the hardness, but relieves, in a greater or less degree, the strains set up in hardening and makes for uniformity as well as more pronounced physical properties.

Annealing after case carbonizing is a doubtful operation. The physical improvement with single heat treatment may be obtained by resorting to double heat treatment, for the results will be better and the time consumed in the operation much shorter. Annealing does not improve the double heat treated pieces and may even cause loss of strength and toughness, due to the decarbonization which may take place. Annealing is not to be recommended.

The case-carbonized steel will, with either double or single heat treatment, become file hard at temperatures too low for the best development of the maximum strength and toughness. Although seemingly paradoxical, the dual nature of the steel after case carbonizing will explain this established fact, when one recalls that the transformations of the exterior are first completed at low temperatures, and that those of the interior are last completed at higher temperatures.

All steels lose their file hardness when drawn at 425 degrees Fahrenheit, save chrome canadium which loses it at 450 degrees Fahrenheit.

The ideal heat treatment for a case carbonized steel may be assumed to be: Case carbonize to the thinnest possible depth of case demanded by the conditions of service; reheat for the core: quench in a suitable fluid; draw the temper as far as the conditions of service will permit.

Case-carbonized steel parts, such as gears, etc., may be stronger, tougher and harder than similar parts made from oil hardened steels.

A micrscopic experiment on the effect of heat treatment after case carbonizing was to determine, if possible, the constitutional difference between a case-carbonized bar of steel which had received a single heat treatment, and a piece of the same metal carbonized in the same manner which had received a double heat treatment, the first reheating designed to be the best possible for the interior of the core, and the second reheating designed to be the best possible for the case or carbonized zone. The results indicate that the double heat treatment increases the strength and toughness of case-carbonized steel due to the smaller and finer martensitic structure developed.

TEMPERATURE IN CASE HARDENING.

The object of another experiment was to determine the lowest temperature at which case carbonizing begins; the lowest temperature with each of the three different types of case-carbonizing steels (straight carbon and alloy are of the same carbon content) at which it might be most efficiently conducted in practice; and the best temperature for the case carbonizing of steel.

The following is a general summary of conclusions of temperature in case carbonizing:

The depth of case carbonizing effect in a given time increases with the temperature.

The carbon content in the case-carbonized zone in a given time increases with the temperature. This affords the commercial opportunity of varying the depth of case-carbonizing effect as desired by changing the time, and of varying the carbon content of the case-carbonized zone by changing the case-carbonizing temperature. It is poor practice to raise the temperature of the case-carbonizing operation for the purpose of reducing the time which the operation consumes, for this will increase the maximum carbon content of the case-carbonized zone and may change the character of the physical properties of the finished product.

The minimum temperature at which uniform penetration of carbon can be obtained with case carbonizing seems to be 1500 degrees Fahrenheit. With lower temperatures the carbon maximum is not uniform in its distribution and the penetration too slow.

The presence of excess cementite in the form of needles within the pearlite grains, so conspicuous in nickel and carbon steels, indicates a temperature during case carbonizing which overheats the metal being so treated.

NICKEL AND CHROME VANADIUM.

Nickel steel gives the greatest total penetration and greatest gradation zones.

Chrome canadium gives the highest carbon maximum and finest grained steel.

When case carbonizing is conducted at 1400 degrees Fahrenheit, or lower, the carbon maximum does not exceed the eutectic. As the case-carbonizing temperature increases, a zone of hypereutectic composition develops which increases in depth with the temperature. The depth of this zone becomes important when sufficient warpage takes place in the piece being hardened to demand grinding after the final heat treatment. It has been demonstrated often that a carbon content of more than 1 per cent. in the surface of a case-carbonized part is undesirable when there is the least shock to be reckoned with, because in such instances the excess of carbon exists in the form of films of carbide between the grains of the metal which are brittle and hard, weakening the steel and rendering it liable to fail by flaking off or spawling. Therefore it would be inadvisable to select a practice or a material which produces such a condition in the surface. On the other hand, if the carbon percentage is lower than 0.90 to 1.00 per cent., the case will not show its maximum hardness. Therefore, when pieces are to remain unground practice should aim at a production of a 0.90 per cent. carbon surface, but when a portion of the steel is to be ground off, after the heat treatment, it is advisable to drive in an excess of carbon so as to leave this optimum percentage at 0.9 to 1.00 per cent. in the final surface.

All carbonized zones widen with increase of temperature. While wide gradation zones are desirable

from the point of view of tenacity of the case to the core, other considerations enter into the commercial side of the problem. The first is the cost of maintaining the high heats. The factors of fuel cost and increased furnace upkeep cost at the upper temperatures are self-evident. The second is the difference in the nature of the case. Inspection will show that at 1500 degrees Fahrenheit the width of the eutectic zone is considerably greater than that of the hypereutectic zone and the hypoeutectic zone of the decreasing carbon content is wider still, which means, of course, that the case carbonizing is proceeding gradually and that the case and core are merging into each other by gentle degrees. At 1600 degrees Fahrenheit the ratio of the high carbon exterior zone to the inner zones rises, and at 1700 and 1800 degrees Fahrenheit the increase is more marked still.

THE LESSON THAT WAS LEARNED.

The meaning of all this is, that as the temperature goes up carbon is forced by the heat, as it were, to rush into the surface of the steel faster than it can be assimilated by the adjacent grains and so the outside layers at the high heats are gorged with carbon which has not time to diffuse gradually toward the center of the case. This condition of affairs is highly undesirable, because the product then shows a sharp demarcation between case and core, the transition from one material to another being too abrupt; the properties necessarily vary accordingly and in the finished piece have a tendency to set up high physical strains. This causes flaking off of the case from the core, a phenomenon familiar enough to those engaged in the trade. The remedy is to case carbonize at a moderate heat for a length of time sufficient to obtain a reasonable depth of case with gradual transition from case to core. This temperature appears in this experiment to be about 1650 degrees Fahrenheit, with open-hearth carbon steel, 1600 degrees Fahrenheit with electric nickel steel and 1650 degrees Fahrenheit with electric chrome canadium steel.

In deciding upon the best carbonizing temperature the effect of heat on the size of grain in the steel must also be considered. This, as is well known, is a very decided reaction, the grain coarsening rapidly with increasing temperatures. In this connection a careful investigation showed marked contrast between the behavior of ordinary carbon steel and the two alloy steels; the former began to coarsen rapidly at 1500 degrees Fahrenheit; nickel steel also showed the same effect at the same temperature, but in a much less marked degree and chrome vanadium steel retained its fine grain up to 1700 degrees Fahrenheit and over, not reaching, even at 1800 degrees Fahrenheit, the grain size of other steels. This is in line with the common belief that chromium and vanadium retain fineness of grain in steel.

CHEMICAL ANALYSIS FOR DEPTH.

Another experiment was to determine by chemical analysis the depth of carbonizing effect and carbon content of several zones of carbonizing effect as affected by the composition of steel under treatment. The information obtained indicated that the higher the carbon content of the steel case carbonized, the higher will be the maximum carbon content of case when case carbonizing is performed at a given temperature for a given time; the original carbon content does not affect the depth of case under the conditions of this experiment; the nickel and carbon steels behave similarly in regard to carbon maximum. Chrome vanadium steel takes a higher carbon maximum than nickel steel and carbon steel under the same case-carbonizing conditions.

A most instructive experiment to determine the commercial efficiency of case-carbonizing materials and the elements which affect their value commercially, fourteen of those materials being selected for the purpose. The results follow:

As these materials are used by volume, not by weight, this volume per ton must be considered in the economic purchase of this grade of material.

All the compounds show shrinkage of volume and in most instances a loss of potency with continued service. This point is of greatest commercial interest since, if steel of variable carbon content is produced in the case-hardening process, the manufacturer cannot hope for uniform results.

With the compounds on the market, any desired maximum carbon content in the case can be obtained with a given temperature simply by varying the compounds used.

When parts are produced which require grinding after treatment, a compound should be selected which gives a high maximum carbon content.

When parts are produced which require resistance to shock after heat treatment, a compound should be selected which gives a carbon maximum sufficient for the hardness desired and not in excess of this amount, or brittleness will result.

The ideal case-hardening compound, as indicated by the experiment, would possess the following characteristics: (1) large volume per ton; (2) small shrinkage per run; (3) high resistivity to change of shape or powdering; (4) cleanliness and freedom from dust; (5) uniform case-carbonizing power at all runs; (6) capability of being used an innumerable number of times.

The information herein presented was obtained with the object of pointing out; (*a*) the quantitative effect of the commercial irregularities which creep into case-carbonized steel parts; (*b*) the precautions which must be observed if uniformity is desired; and (*c*) the physical characteristics in case-carbonizing materials which must be considered if low cost for this operation is to be obtained.

The ideal case-carbonizing compound perhaps has not yet been produced; however, compounds which are clean, mechanically strong, uniform in case-carbonizing power and capable of unlimited reuse are being commercially employed in case-carbonizing operation.

HYPOCHLORITE SOLUTIONS FOR BLEACHING AND DISINFECTING PURPOSES.*

By JOHN B. C. KERSHAW.

CHEMICAL METHODS OF PREPARING HYPOCHLORITE SOLUTIONS.

Bleaching powder is the raw material used as the base of all chemically prepared bleaching or disinfecting hypochlorite solutions, and from this chemical it is possible to produce solutions of any degree of concentration of active chlorine, and of any chemical composition. This is a fact sometimes ignored by supporters of the electrolytic processes, who assume that only solutions of calcium hypochlorite can be prepared from bleaching powder, and overlook the fact that by double chemical decomposition, quite a series of other salts can be prepared from this base, all of bleaching or disinfecting value.

Calcium Hypochlorite.—The usual method of preparing bleaching solutions is to treat the bleaching powder with water in a vat provided with a stirring apparatus, and to draw or siphon off the supernatant liquor, after allowing the insoluble calcium carbonate, hydrate and other impurities time to settle. The residues ought to be washed twice with fresh water, and the washings used for reducing the stronger liquor to the strength required for the bleaching operation. If a series of three vats be provided, connected in the same manner as those used for the lixiviation of black-ash, with some device for reducing to powder all the larger lumps of bleaching powder before they are put into the vat, the most satisfactory and economical results can be attained, and 95 per cent of the available chlorine in the bleaching powder should be recovered in the liquor produced. The solutions used for bleaching cotton goods should test from ½° to 3° Tw.

Sodium Hypochlorite.—By treating bleaching powder with sodium carbonate or sodium sulphate, the hypochlorite of lime is converted into the corresponding sodium salt, and a liquor similar in composition to that produced by the electrolytic process is attained.

The following methods of manufacture may be used:

I. Method with Soda Ash (Sodium Carbonate).—638 lbs. of bleaching powder are ground to a paste with 242 gals. of water. To this paste is then added 385 lbs. of soda ash dissolved in 110 gals. of water, and the resulting solution is at once made up to 440 gals. The mixture is stirred for half an hour, and is then allowed to settle for twelve hours. The clear supernatant liquor is then drawn off, and the residue is washed twice with fresh water until the total solution measures 1,100 gals. The solution obtained should test 6° to 6½° Tw., and be slightly alkaline. The liquor is said to keep well, and when required for use is treated with sulphuric acid in the proportion of 6 to 7 grs. of the former acid (1.71 sp. gr.) to every litre of liquor (Thies and Herzig).

II. Method with Saltcake (Sodium Sulphate).—Dissolve 14 cwts. of saltcake in 1,020 gals. of hot water, neutralize the free acid with a few pounds of soda ash and allow the solution to cool. Then add 18 cwts. of bleaching powder finely ground, and mix thoroughly with the solution of saltcake by mechanical agitation. The mixture is now run on to a vacuum filter, constructed with a bed of the following grades of limestone:

Top.—2 ins., lumps of 2 ins. diameter.
Middle.—8 ins., lumps of 1 to ½ in. diameter.
Bottom.—2 ins. fine limestone.

The precipitated calcium sulphate is well and rapidly separated by this filter, and the whole of the mixture should be filtered before washing is started. The strong liquor obtained amounts to about 740 gals., testing 21° Tw., or 6½ per cent available chlorine. The residual mud on the filter is then washed three times with the least possible quantity of water, and the washings are added to dilute the stronger liquor to the strength required for use.

The loss of available chlorine in the mud depends upon the quantity of water used for washing and upon the number of washes given; it should be under five per cent of that present in the original bleach. Expressed in tons and decimals of a ton, the quantities required for this method are: *Bleach,* 1 ton; *saltcake,* .80 ton; *soda ash,* .07 ton.

Magnesium Hypochlorite.—Magnesium hypochlorite can be produced by similar methods, but the early claims relating to the greater bleaching efficiency (for equal amounts of available chlorine) of this salt have not been substantiated by the latter researches, and electrolysers are now seldom operated with magnesium chloride or with sea water in order to produce this form of hypochlorite. The Hermite cell is, in fact, the only one which is still operated with a mixture of sodium and magnesium chlorides as electrolyte, and in this case the gain in efficiency is disputed by many who have studied the published figures. Any gain that results from the use of magnesium in the cell is probably due to the formation of a skin of magnesium hydroxide at the cathode. This coating tends to prevent reduction of the hypochlorite by the nascent hydrogen liberated beneath it at the face of the cathode.

ELECTROLYTIC METHODS OF PREPARING HYPOCHLORITES.

(*a*) *General Principles and Charles Watt's Original Cell.*—When a solution of sodium chloride is electrolysed, with a current of suitable strength, using insoluble carbon or platinum electrodes, the following reactions occur:

1.—$6NaCl = 6Na + 6Cl$.
(Cathode) (Anode).

2.—$6Na + 6H_2O = 6NaOH + 6H$.
(Nascent).

3.—$6Cl + 6NaOH = 3NaOCl + 3NaCl + 3H_2O$.

Equation 1 represents the electrolytic action due to the passage of the current; equations 2 and 3 repre-

*From the Chemical Trade Journal and Chemical Engineer.

sent the secondary (or chemical) reactions which result in the production of hydrogen gas, sodium chloride, sodium hypochlorite and water. Two molecules of salt thus yield only one molecule of hypochlorite; the other free atom of chlorine reverting to the state of chloride. The above reaction only occurs satisfactorily, however, below 25° C.; if the solution becomes heated above this limit chlorate is produced. The conditions necessary for the formation of hypochlorite in an electrolytic cell are therefore: (1) Insoluble electrodes; (2) absence of a diaphragm; (3) low temperature of the electrolyte; (4) rapid circulation of the electrolyte; (5) electrodes in close proximity, preferably with the cathode above the anode.

It is of historical interest to note that Charles Watt, in his remarkable Patent No. 13,755, of 1851, was the first electro-chemist to recognize that hypochlorites and chlorates could be produced by the electrolysis of sodium chloride solutions, in a cell provided with insoluble electrodes.

In the third section of this patent he describes the form of cell that he used for decomposing alkali chloride solutions, and the nature of the chemical changes that occur, in the following words:

"A warm solution, and nearly saturated, of the chloride of potassium or other chloride to be operated upon is prepared and placed in a vessel furnished with two electrodes, and in Fig. 4 I have shown a vessel furnished with a pair of electrodes and constructed in such a manner as to be convenient for carrying this part of my invention into effect. In this figure (B) is the interior of the vessel, which is furnished with a steam jacket A, with connection to a boiler (*a*) and waste steam tap (*d*): G, thermometer; E E, electrodes placed over each other, the lower one being intended for the elimination of the chlorine, and the upper one for the elimination of the alkali; *e e*, attachments of the electrodes. I have found it advantageous to add to the solution of the chloride a portion of free alkali, or alkaline earth, equal to about one-tenth of the quantity of the saline matter to be decomposed. The connection is now to be completed between the apparatus which supplies the electric current, or currents, and the vessel, and if the object be the formation of chlorate I maintain the action until from one-half to two-thirds of the original saline matter shall be converted into a chlorate. The agency of the electricity first decomposed the chloride, the chlorine being eliminated at one of the electrodes, and the alkaline or earthy metallic base at the other electrode. The metal thus set free from its combination with chlorine combines with oxygen, and so becomes converted into an oxide; the oxygen being obtained from the water of the solution, a portion of which is therefore decomposed and hydrogen gas evolved; and this gas may be allowed to pass away or, if desired, collected in another vessel. The liberated chlorine will, when it is set free, combine with a portion of alkali or alkaline-earth in solution, and a hypochlorite will be formed."

After describing the chemical changes that occur when chlorates are formed, Watt next describes the conditions required to produce hypochlorites as follows:

"If I desire to produce a hypochlorite of the alkali or earth, I merely keep the vessel warm (say from about 100° to 120° Fahr. thermometer) without applying the higher temperature, which it is well known is requisite to produce a chlorate from a hypochlorite; and I continue the process until as much as the saline matter has been converted into a hypochlorite as may be required for the purpose to which the solution is to be applied. This mode of forming a hypochlorite of the alkalies and alkaline earth may be used for preparing a bath for the purpose of bleaching various kinds of goods, and the bath may be strengthened from time to time by the action of the electric current or currents."

The fourth section of Watt's 1851 Patent relates to the use of electrolysis for separating and refining metals, but in the above extract Watt showed that he had a clear grasp of many of the more important details, upon which the formation of hypochlorite and chlorate in the electrolytic cell depends.

The Haas and Oettel Electrolyser.—The latest form of this electrolyser makes use of carbon as electrode material, and of the liberation of hydrogen gas at the cathode to effect automatic circulation and mixing of the liquid in the cell. In this electrolyser the inner or working cell is a rectangular stoneware tank divided by the carbons into thirty narrow compartments or cells, each of these subsidiary cells having one hole at the bottom and two others at the sides, about 2 ins. from the top. The first and last carbons of the set form the main electrodes of the cell; the intervening carbons act as secondary electrodes, functioning as anodes on the one face and as cathodes on the other. This inner cell is supported on a brick foundation, within a stoneware tank measuring 72x48x36 ins. deep, and is filled with a 15 per cent solution of brine to within 4 ins. of the top. The carbons are protected at their top and bottom edges with slips of glass of the same width as the carbons—these prevent short-circuiting due to dirt and sludge, and also prolong the life of the carbons. A direct current of 80 amperes at 110 volts is employed to work this electrolyser. As soon as electrical connection is made, the evolution of hydrogen at the negative or cathode surface of the electrodes causes the level of the liquid within the cells to rise above the overflow pipes, and a rapid circulation of the brine occurs, fresh liquor flowing in at the bottom of the cells. The liquor passing away at the top of the cells passes over cooling plates to reduce the temperature, and when necessary the heat produced by electrolyses is further dispersed by the aid of cooling pipes placed in the larger containing tank.

The following figures give the yields of the industrial type (T E/3) of this electrolyser:

Capacity.—750 litres of brine. Strength 15 per cent. Salt required, 112.5 kgs.

Current.—75 to 80 amperes at 110 volts, for ten hours, equivalent to 88 B. T. U. (Board of Trade units).

Yield.—750 litres hypochlorite solution, containing 14 grs. free Cl. per litre, equivalent to 10.5 kgs. Cl.

The carbon electrodes are reported to have a life of eighteen months for a ten-hours working day, and to cost for renewal £6. 10s. per set. The labor required for operating this type of electrolyser is about one hour per day, as when once charged with fresh brine it can be left for ten hours with but slight attention. The current efficiency falls from 95 to 52.8 per cent during the ten hours required to produce a solution containing 14.0 grs. Cl. per litre, the highest efficiency, 90 to 95 per cent, being obtained with a concentration of 2.5 grs. Cl. per litre. The cost of the complete electrolyser, type T E/3, is £150.

The Kellner Electrolyser.—This electrolyser consists of a shallow stoneware tank, divided into a large number of narrow cells by means of vertical glass plates, so arranged that the electrolyte is obliged to take a horizontal zig-zag course in its passage through the electrolyser. The electrodes are formed of platinum-iridium gauze, and are arranged horizontally with the anodes below the cathodes, so that the chlorine liberated at the former may be absorbed by the supernatant liquid.

This electrolyser has only two terminal electrodes. The intervening electrodes function as secondary electrodes as in the Haas and Oettel apparatus. The electrolyser is constructed usually to take a current at 110 volts. Brine is passed continually through the apparatus until the desired concentration of chlorine is attained, a small centrifugal pump being employed to circulate the brine through the electrolyser, and an external cooling vessel being used to keep down the temperature below 25° C. Using a 10 per cent solution of salt the current efficiency falls from 87.5 to 45.9 per cent in ten hours, the free chlorine rising from 3.09 to 12.95 grs. during this period. The following figures give the yield of the industrial type (2ESn 60/9) of this apparatus:

Capacity.—600 litres of brine. Strength 15 per cent. Salt required, 90 kgs.

Current.—90 amperes at 110 volts for ten hours, equivalent to 99 B. T. U.

Yield.—600 litres of hypochlorite solution, containing 25 grs. free Cl. per litre, equivalent to 15.0 kgs. Cl.

Cost.—£300, with platinum at £200 per kilog. (124s per oz.).

The life of the platinum iridium electrodes is, of course, much longer than that of the carbon electrodes employed in the Haas and Oettel electrolyser, and their scrap value is considerable; but on the other hand they are not absolutely indestructible, and if the brine contains magnesium or lime salts, deposits of these may cause trouble.

The Hermite Electrolyser.—The distinctive features of this cell and process are the use (1) of a mixture of sodium and magnesium chloride as electrolyte; (2) of magnesium hydrate as a preservative; and (3) of zinc as negative element in the cells. The electrolyte is prepared in an elevated tank, and is allowed to flow by gravity through a series of four double troughs, which form one unit of the Hermite plant at Poplar. These troughs were formerly made of slate but are now constructed of glazed earthenware, and each is divided by a partition which causes the electrolyte to pass horizontally twice along the length. Each division or cell contains five sets of electrodes, two negative electrodes of zinc enclosing one positive electrode, formed by winding thin platinum wire upon a perforated porcelain slab of the required shape. There are thus eight separate cells, containing forty pairs of electrodes in the one unit of plant, and a current of 15 amperes at 230 volts is employed, the electrodes and cells all being connected electrically in series. The electrolyte passes between each of these electrode pairs in its passage from the inlet to the exit, the flow from one trough to the next being controlled by glass syphons and funnels. A small addition of magnesium hydrate solution is made to the liquid as it flows from the last trough, glass carboys being employed to receive the mixed solution of sodium and magnesium hypochlorites. The capacity of each unit of plant is 185 to 200 gals. of solution, at a strength of 4 to 6 grs. Cl. per litre, per 2-hour day, the rate of flow of electrolyte being 3 1-3 pints per minute. The first unit of plant at Poplar was erected at the beginning of 1906 and cost, with all the necessary accessories, £583; the second unit erected at the beginning of 1910 cost £501. The running cost, electricity, water, chemicals, supervision and testing, for the half year ending September 30, 1910, amounted to £100, but this total does not contain any allowance for interest, depreciation, rent, or distribution charges.

The net cost of one Hermite electrolyser is £325.

(e) The Vogelsang Electrolyser.—The original form of Vogelsang electrolyzer resembled, in its main constructive features, the earlier Hermite and Kellner electrolyzer, the electrolyte being made to take a vertical zigzag course through a trough filled with a large number of secondary electrodes. Lead plates faced with platinum on the anode side were used as the intermediate electrodes, and by varying the number of these the electrolyser could be made to take a current of 85 amperes, at 65 or 110 volts. An electrolyser of this tye was said to have produced 20 kgs. of active chlorine in a 10 hours working day, equivalent to a yield of 1 kg. active chlorine per 6.6 E. H. P. hours, or an energy efficiency of 35.8 per cent. The use of lead for electrodes did not, however, prove satisfactory, and the Vogelsang cell has been considerably modified. The electrolyser now worked at Nottingham and other places abroad is constructed with composite electrodes. Narrow bars of slate, extending the

full width of the cell, are wrapped with a sheet of platinum-iridium foil in zigzag fashion, the result being a composite electrode of great strength, which can carry high current densities, and presents opposing surfaces of foil where required. An important consideration in this method of electrode construction is to arrange that the sectional area which is allowed for carrying the current through the electrode (from one face to the other) is proportioned to the superficial electrode surface in contact with the electrode.

(*f*) *The Mather and Platt Electrolyser.*—This electrolyser resembles that of Kellner, and is constructed with thirty-nine electrodes made of a platinum-iridium alloy, and with two terminal electrodes for connection to the current mains. The forty cells into which the electrolyser is divided by plate-glass strips are so arranged that the electrolyte takes a zigzag course, and attains a strength of 7 grs. Cl. per litre at the exit of the electrolyser. A current of 191-3 amperes, at 220 volts for ten hours, is stated to yield 7 kgs. active chlorine, equivalent to 6.07 kw. hours per kilog. of active chlorine. The strength of the salt solution used is 6 per cent. and cooling tanks are employed both for the brine and the electrolysed liquor.

Taking the figures given in the above descriptions of the various forms of electrolytic hypochlorite cell, and bringing them to a common basis of comparison, we obtain the following figures for their relative yields and efficiencies:

Type of Cell.	Salt Used.	Kw. Hrs.	Active Chlorine in Kgs.
Haas and Oettel..	112.5 kgs.	$\frac{80\times110\times10}{88}$	10.5 kgs.
Kellner	90.0 kgs.	$\frac{90\times110\times10}{99}$	15.0 kgs.
Hermite	35.7 kgs. NaCl 10.8 kgs. $MgCl_2$ equal to 49.00 kgs. NaCl	$\frac{15\times230\times8}{27.6}$	4.35 kgs.
Mather and Platt..	.....	$\frac{19.33\times220\times10}{42.52}$	7.00 kgs.
Theory demands..	0.947 kg.	1.00	0.574 kg.

Results expressed as kgs., salt used and kw. hours consumed per kilog. of active chlorine obtained.

	Salt Used. Kgs.	Salt Used. Percentage Decomposed.	Power Used. Kw. Hrs.	Energy Efficiency
Haas and Oettel.....	10.70	15.5%	8.4	21.0%
Kellner	6.00	27.5%	6.60	26.5%
Hermite	11.20	14.5%	6.31	27.0%
Mather and Platt....	....	....	6.07	28.6%
Theory demands.....	1.65	100%	1.74	100%

These figures show that the Hermite and Mather and Platt cells are the most efficient as regards power consumption, and that the Kellner cell is the most economical in salt; although in neither case is a working efficiency of 30 per cent attained. The superior energy of the Hermite cell is chiefly due to the fact that the hypochlorite solution finally obtained has a concentration of only 5 to 6 grs. free Cl per litre, as compared with 14.0 grs. for the Haas and Oettel electrolyser, and 25.0 grs. for the Kellner type of cell. As already stated the current efficiency of any hypochlorite cell diminishes rapidly as the electrolysis proceeds, due to the secondary reactions which are inherent to all processes of this character.

COMPARATIVE BLEACHING EFFICIENCIES OF CHEMICAL AND ELECTROLYTIC CHLORINE.

The early claims that were made for the superior bleaching efficiency of chlorine produced by electrolytic methods have been modified by the results of recent independent research, and it is now generally accepted that there is but slight difference (not exceeding 5 per cent) between the bleaching effects obtained if the chlorine be present in the same form of combination and in the same degree of concentration in the various bleaching liquors.

The following are summaries of the results obtained in the most recent and reliable researches upon this question of relative efficiency.

Fraas, in a paper published on June 15, 1909, in the *Zeits. f. Elektrochemie,* gives details of the results of an investigation of the bleaching effects of chemically and electrolytically prepared chlorine upon cellulose. The special points investigated were: (1) Which of the two bleaching agents gives the better color when using similar amounts of chlorine; (2) what saving in chlorine or bleaching agent is possible when obtaining equal bleaching effects; (3) what influence have variations in the acidity of the souring liquors upon the results; (4) what influence has an excess of bleaching agent upon the results.

A total of forty-nine experiments were made during the investigations, and the results of these are set forth in four tables, to be found in the original paper.

The results are summarized by the author as follows: (1) Using equal amounts of chlorine, and working under similar conditions, the electrolytic bleaching liquor gives the better bleaching effect; (2) if the bleaching effect be stopped at the same degree of whiteness, the use of electrolytic liquor enables a saving of 5 per cent of chlorine to be made when working with alkaline solutions; (3) the presence of an excess of bleaching liquor does not alter these comparative results; (4) increase of alkalinity diminishes the rate of bleaching, but increases the final effectiveness of the bleach in the case of both electrolytic and bleaching-powder solutions.

Higgins, in a paper read and discussed before the Society of Chemical Industry (Manchester Section), on January 6, 1911, and published in the issue of the Journal of that Society for February 28, 1911, gives details of bleaching experiments made with solutions prepared in three different ways, and cotton or linen yarn and cloth. The first solution was one of sodium hypochlorite, containing 15 grams of free chlorine per litre, obtained by electrolysis of an 11 per cent solution of brine; the second was a solution of calcium hypochlorite of 1.08 sp. gr., obtained by treating ordinary bleaching powder with water; the third was one of sodium hypochlorite, obtained by treating the last solution with sodium carbonate until no further precipitate of calcium carbonate was obtained. The re-

sults are given in Higgins' own words, as they are of considerable importance in their bearing upon the subject of this article:

"*Stability of the Bleaching Liquors.*—Large quantities of these three liquors were made up to about the same chlorine contents and allowed to stand in air, small samples being titrated with decinormal sodium thiosulphate solution at intervals, to ascertain their rates of decomposition. At the same time electrochemic of one-half and one-tenth the original strength, and calcium and sodium hypochlorites of one-tenth the original strength, were allowed to stand. Some evaporation took place during the five days, but this was about the same for all samples. It was proved that there was practically no difference between the stabilities of the three liquors; the electrochemic being as the chloride of lime solution.

"*Effect of Prolonged Agitation on the Liquors.*—It has been said that electrochemic must be carefully handled, syphoned, and not agitated, as it readily decomposes. This, however, is not the author's experience. Shaking the three liquors in flasks for many hours did not cause appreciable decomposition.

"*Bleaching Effect of the Liquors.*—The three strong liquors, after standing five days, were diluted to half strength with water, and into 1½ litres of each, 35 grams of brown linen cloth were placed. At intervals the solutions were tested to give Table II. 10 c.c. of liquor was titrated in each case. The figures show that there is practically no difference between the rates of bleaching of the three liquors. The bleaching powder solution bleached as rapidly as the electrolytic liquor.

"*Tensile Strengths of the Yarns after Bleaching.*—The linen cloth used in the previous experiments was taken from the same piece. After the bleaching the pieces were washed, soured, well washed and dried. The pieces were then separated into warp and weft yarns, and these were broken in a Schopper testing machine. In order to get a good average strength, thirty yarns were broken in each case. There was no difference between the action of the electrochemic and of the other bleaching solutions.

"During the bleaching the liquors became milky in all three cases, and to about the same degree. Acid was required to clear the cloth in all cases. The samples of cloth were approximately the same color after the bleaching; one sample could not be distinguished from another. The electrochemic and other chlorine solutions were found difficult to wash out from the cloth. This is also the case on the large scale where (*e. g.*) the salt from the electrochemic is readily washed out of the cloth, but the last traces of chlorine are difficult to remove.

"It has been said that when bleaching powder solution is used for bleaching the goods have a harsh feel, but this is merely due to lack of souring or proper washing. Souring leads to the production of calcium chloride or sulphate, which, if left in the cloth, cannot produce harshness, for calcium chloride is sometimes used along with starch to give a full soft finish.

"*Stability of Sodium Hypochlorite Solution on the Addition of Caustic Soda and Common Salt.*—Calculations showed that the electrochemic used in the previous experiments contained about 120 grams of undecomposed salt per litre. This quantity of salt was added to the sodium hypochlorite solution to ascertain the effect on the stability of the solution. At the same time 10 grams of caustic soda were added to 1 litre of the hypochlorite. These liquors were allowed to stand in air and gave the following results, 5 c.c. of liquor being titrated with thiosulphate in each case. (The figures show only slight change, even at the end of sixty-six hours).

"*Rate of Bleaching of Sodium Hypochlorite Solution Containing Salt and Caustic Soda.*—Into the solutions at the end of the previous experiments 28 grams of linen cloth were placed, and the same amount into a litre of sodium hypochlorite solution of the same strength as the other liquors. The liquors were tested as before, 5 c.c. being titrated with thiosulphate in each case.

"The figures show that the addition of common salt in large quantity to sodium hypochlorite solution slightly decreases its stability and increases its bleaching effects. This change, however, is so small as to be of no practical use. Caustic soda, as expected, increases the stability and decreases the rate of bleaching of the hypochlorite."

Summarizing these results, it may be stated that Higgins found there was but slight difference between the bleaching efficiency of the two solutions or between the quality and durability of the goods bleached in the two different ways, and that the higher efficiency claimed for the electrolytic hypochlorite solutions was not supported by the results of his experiments. The discrepancy between his results and those obtained by earlier investigators was, no doubt, due to the fact that other salts in solution have, as Higgins points out, considerable influence upon the rapidity with which the hypochlorite gives up its oxygen to the coloring matter of the yarn or cloth.

COMPARATIVE COST OF CHEMICAL AND ELECTROLYTIC CHLORINE.

The costs of power, raw materials and labor differ so much in various districts and localities that no very decisive general figures can be given for the relative costs of the chemical and electrolytic methods of preparing bleaching liquors. Each case in which it is proposed to adopt one or the other must be judged with the actual figures for the local costs before one. The following estimate is for a small bleaching installation in South West Lancashire, within fifty miles of the Cheshire salt field, with cheap fuel, chemicals, and labor all at hand. The figure for power costs, namely, .425d per unit, has been obtained from the Chief Engineer of the City of Manchester Electricity Undertaking, and represents what would be charged to

a consumer for a steady load of 80 to 100 units per day. It is certainly doubtful if any small private installation in S. W. Lancashire could produce at so low a figure. The amounts charged for depreciation of the electrolysers is small, but glazed earthenware containing vessels and platinum electrodes should have a long life, and with proper care 2.5 per cent depreciation on the whole electrolyser plant should be sufficient to meet the costs of necessary renewals.

(*a*) CHEMICAL METHODS.

(1) *Calcium Hypochlorite.*—Taking 35 per cent bleach at £4 12s 6d per ton, d/d, and assuming that 5 per cent of the Cl is lost in making up the bleach solution, the cost per ton of active chlorine will be as follows:

	£	s.	d.
3 tons bleach at £4 12s 6d per ton	£13	17	6
Labor, eight hours, one man	0	4	6
Interest and depreciation on plant, 10% on £100	0	0	8
	£14	2	8

(2) *Sodium Hypochlorite.*—(*a*) Using soda ash at £4 5s per ton, d/d, to decompose the calcium hypochlorite solution, the cost per ton of active chlorine will be as follows, assuming as before that 5 per cent of the chlorine is lost in the process:

	£	s.	d.
Bleach, 3 tons at £4 12s 6d per ton	£13	17	6
Soda ash, 1.9 tons at £4 5s per ton	8	1	5
Fuel, 5 cw'ts. at 10s per ton	0	2	6
Labor, two men, eight hours	0	9	0
Interest and depreciation on plant, 10% on £200	0	1	4
	£20	5	1

(*b*) Using saltcake at £2 2s 6d per ton, and soda ash at £4 5s per ton, to decompose the calcium hypochlorite solution, the cost of active chlorine per ton will be:

	£	s.	d.
Bleach, 3 tons at £4 12s 6d per ton	£13	17	6
Saltcake, 2.4 tons at £2 2s 6d	5	2	0
Soda Ash, 3 cwts. at 4.25s per cwt	0	12	9
Fuel, 5 cwts. at 10s per ton	0	2	6
Labor, two men, eight hours	0	9	0
Interest and Depreciation on Plant, 10% on £200	0	1	4
	£26	5	1

B.—ELECTROLYTIC METHODS.

Taking the best results in the table of comparative efficiencies already given, namely, 6.07 k.w.-hrs. and 6.0 kgs. salt per kilog. of active chlorine; 15 kgs. Cl per 10 hr. day, the Manchester Corporation charge for electric power, and salt at 16s 6d per ton—we obtain the following as the estimated cost of one ton of active chlorine by the electrolytic method of manufacture in South West Lancashire:

	£	s.	d.
Power: 6070 kw. hrs. at .425d	10	11	11
Salt: 6000 kgs.=6 tons at 16s 6d	4	19	0
Labor: 66 hrs. at 6d per hour	1	13	0
Depreciation: 2.5% on £300 for 66 days	1	10	0
Interest: 5% on £300 for 66 days	3	0	0
	£21	16	11

The relatively high charges for labor, interest, and depreciation are due to the fact that an electrolyser costing £300 would only produce 15 kgs. active Cl per day of 10 hrs., and that it would require to be worked for 66 days continuously to produce 1000 kgs. or one metric ton of active chlorine. The labor, interest, and depreciation charges therefore cover this period, or one-fifth of a working year. These charges could not be materially reduced by enlarging the plant, and producing one ton of active chlorine per week, for the capital outlay would then be correspondingly increased, and the only saving would be a small one in wages for labor. In order to show that this estimate of the cost of one ton of active chlorine by the electrolytic method is not incorrect, the following figures from an article by Dr. Engelhardt, one of the chief technical engineers in the Electrochemical Department of Messrs. Siemens and Halske's Werner Works at Berlin, may be given.

Dr. Engelhardt's estimate with power at .250d per kilowatt-hour works out to £18 16s per ton of active chlorine for a small plant producing 48.9 lb. active chlorine per day of ten hours, and correcting this estimate for power at .425d per kilowatt-hour, we have a total cost of £23 0s 6d for the ton of active chlorine by the electrolytic method.

It is of interest to compare with these two estimates the actual working costs of the electrolytic hypochlorite installation at Poplar, as given in Dr. Alexander's annual report for the year 1910; although in this case the costs of raw materials and of electricity are increased owing to the fact that magnesium chloride and sodium hydrate are used, in addition to sodium chloride, for preparation of the electrolyte, and that electric power costs at Poplar 1½d per unit. During 1910, 50,726 gals. of hypochlorite solution were produced, at the following cost for power and raw materials:

	£	s.	d.
Electricity (8,084 units at 1½d per unit)	50	10	6
Magnesium chloride (5 tons 3 cwt. 38 lb.)	21	6	4
Sodium chloride (9 tons)	15	8	0
Caustic soda	9	7	6
Water	1	10	0
	£98	2	4

Taking the average strength of the solution as 5.3 grms. active chlorine per litre, we find that the above expenditure produced 1,218 kgs. of active chlorine: the cost per ton thus working out to £80 10s 2d, without any allowance for labor depreciation or interest.

Summarizing these results, we have the following interesting table of comparative costs:

COSTS PER TON OF ACTIVE CHLORINE.

Method of Preparation.	Form of Combination.	Cost. £	s.	d.	Remarks.
Chemical	Calcium hypochlorite	14	2	8	
"	Sodium hypochlorite	20	5	1	Using salt cake.
"	"	22	11	9	Using soda-ash.
Electrolytic.	"	21	16	11	Kershaw's estimate
"	"	23	0	6	Engelhardt's estim.
"	Sodium and magnesium hypochlorite	80	11	2	Actual cost at Poplar.

Naphtha exports from the United States increased greatly during the year 1912, being about 178,000,000 gals. During 1911 the exports amounted to 77,000,000 gals.

THE MANUFACTURE OF SWEDISH FILTER PAPER.*

By GUSTAF FORNSTEDT.

There are many different qualities of filter paper, depending upon the use for which they are intended, and they range from an ordinary filtering paper for household use to the fine double-extracted, ashless filter paper intended for very particular analytical work. As a rule, the ordinary qualities are machine-made, while, on the other hand, the finer qualities are hand-made.

Machine-made filter paper includes, among other varieties, beer filtering paper, a paper of about 180-pound weight, made chiefly from cotton rags, and used for filtering beer, as well as for the ordinary filtration of water. The paper is cut square and has 1½-inch round holes perforated in each angle for the insertion of four metal bars on which the paper, alternating with perforated zinc plates, is threaded and screwed firmly together. Through these layers of paper and zinc the beer or other liquid is passed at a pressure of about 0.6 atmosphere: the dirt and impurities remain on the paper and the clean and clear liquid passes through.

Machine-made filter paper is used chiefly in the household and for technical purposes, while hand-made filter paper for scientific analyses is of better quality, though of different grades and make, according to the character of the analysis to be made. The paper being more or less quick filtering, it is made with regard to whether a mere purification of the liquid is intended or whether the substances collected on the paper are to be qualitatively or quantitatively determined.

Some qualities of filter paper, as white and gray woolen paper, are made generally in small paper mills which are not equipped with steam boilers. The rag is furnished "raw" in the beaters and beaten free, but care is taken to avoid lumps. The paper is made on a cylinder machine and taken wet on the hasp from where it is cut by hand and hung up for drying. A rough mottled surface is produced by means of a coarse wire cylinder running on the wet paper web, the impression remaining very plainly after the paper is air dried.

The cleanest rag is, of course, used as material for filter paper, and it must be of the best quality and sorted with great care. It is important to pick out buttons and any pieces of metal that may be carried by the rags. In new cuttings from shirt and collar factories, used in the finest qualities, stray pins and needles give rise to much work and trouble. Iron is, of course, one of the worst impurities in a filtering paper.

The rag is boiled with sodium hydroxide (NaOH), because it gives a lower percentage of ash than lime, and for the same reason the old method of bleaching the halfstuff with chlorine is preferred to the use of chloride of lime in bleaching hollanders.

For chlorine bleaching a mixture of manganese, salt and sulphuric acid is used in leaden retorts in about the following proportions:

	Parts.
Binoxide of manganese	8
Sodium chloride	6
Sulphuric acid	5

Usually, however, a greater quantity of salt is used, because it contains a considerable amount of water.

After the rag is boiled, washed and beaten to halfstuff, it is dried in a centrifugal dryer and spread in layers on wooden poles in the bleaching chamber. This chamber is of concrete, lined with wood. After the bleaching chamber is filled with halfstuff the door is closed and chlorine admitted through an aperture in the roof. After all air has been withdrawn from the chamber, it is well sealed, and the halfstuff, after absorbing the chlorine for several hours, is effectively bleached. Of late, in some mills this bleaching process has been considerably simplified. Liquefied chlorine pressed in steel bombs is used. The bomb is placed in hot water on a scale, a valve on top of the bomb, connected to the bleaching chamber with a rubber hose, is opened, and a certain amount of the liquefied chlorine makes its escape in the gaseous form, and is so forced into the bleaching chamber.

The analysis of boiled and bleached halfstuff shows the following ash percentages (silica and lime):

New shirt cuttings, No. 1	0.039
Old linen, white	0.132
Old linen, gray	0.140
Colored cottons	0.177
White cottons	0.107
Sulphite, bleached	0.298
Soda, bleached	0.4

It is, of course, a matter of great importance that the water used in the manufacture of filter paper should be as pure as possible, but it is impossible to avoid some ash-containing matter from being introduced to the halfstuff with the water of manufacture, and in the transportation of the halfstuff and the process of drying. Generally the increase is from 0.02 to 0.05 per cent, depending on the state of the weather and the condition of the water.

The time consumed in beating varies according to the nature of the material. Halfstuff freshly bleached requires longer time than that which has been stored some time. Neither too free nor too slow stuff should be used for filter paper. Stuff that is too slow retards filtration—meaning the time taken for a given quantity of water of a certain temperature to filter through a paper of specific diameter. Paper made of too free stuff fails to keep back the finer grained sediments, such as sulphate of barium, etc.

Among the considerations to keep in mind in the manufacture of filter paper are the rate of filtration demanded, the ash content, resistance to sulphate of barium, fine holes, weight, and impurities.

To produce a filter paper of low ash percentage requires treatment with hydrochloric or hydrofluoric acid

*From Paper.

or a mixture of these acids, which will remove impurities like ferric oxide, alumina, lime, magnesia and silica, and paper so treated is practically a pure cellulose paper. With hydrofluoric acid silica is removed, and with hydrochloric acid the other substances enumerated are dissolved away. After treatment with acids the paper should be thoroughly washed with distilled water, to remove the last traces of acidity.

To test the neutral reaction of the paper after washing, a solution of nitrate of silver is used to advantage. The wet paper is squeezed with the hand over a glass funnel and the water filtered into a test tube. In another test tube containing distilled water a few drops of test solution of nitrate of silver are added, and the same quantity is added to the water expressed from the washed filter paper. The two tubes are then compared against a black background. If not neutral, the water from the filter paper will show an opalescence due to the formation of insoluble chloride of silver from the chlorides remaining in the paper, and further washing is necessary. After this treatment the paper is pressed and hung out in open barns in order to freeze it.

By freezing the paper is made soft and porous, since the ice crystals formed in it serve to drive the fibers apart. Because of this the finest qualities of filter paper only can be made in the winter time in cold countries.

Experiments have been tried of subjecting paper that has been dried in a warm atmosphere to a subsequent freezing operation, in order to impart the desired softness and porosity, but it has been found that paper treated in this way does not become soft, and it never comes up to the standard of the best Swedish filter paper.

Extracted filter paper is practically ashless, the ashes amounting to about 0.015 per cent of the weight of paper, and is often negligible, not being taken into account in quantitative analytical work.

The most careful, accurate work is necessary in any determination of the ash content of a paper. The instruments required consist of a spacious drying apparatus of copper, two exsiccators, one large and one small, a platinum crucible (about 0.7 ounces) with cover, a stand, a spirit lamp, a blast lamp or Bunsen-burner, and a particularly exact balance scale.

The larger exsiccator is used for the dried paper and the smaller for the platinum crucible. Every time the crucible is used it must be cleansed with the finest sand, which has been previously boiled in diluted hydrochloric acid, dried, fired and kept in the exsiccator until the next time it is used. The scale placed on a table fixed to the wall ought to be of superior construction for fine analytical determinations. Soot must naturally be guarded against in the incinerating operation, as the particles would lead to error in the weighing and conduce to an early deterioration of the crucible.

The manipulations are as follows: The sample is first dried in the drying apparatus at a heat of 190° to 210° F. It is then transferred to the exsiccator for 15 minutes, and afterwards cut in small pieces and put in the cleaned and weighed crucible. The crucible is supported on its stand and the cover adjusted so that air may enter. The crucible is first heated red hot, at which point the hydrocarbon volatilizes; the heat is then increased for 20 minutes, until the crucible glows white hot. After the ash turns white or gray-white the crucible is placed in the exsiccator for ten minutes and weighed; the incineration is then continued until a constant weight is obained.

If the crucible weighs *a* gramme, the crucible and paper *b* gramme, and crucible and ash *c* gramme, the following formula is obtained:

Paper and crucible	=	*b* Gm.
Crucible	=	*a* Gm.
Paper	=	(*b*-*a*) Gm.
HAND BRACE—		
		a Gm.
Ash and crucible	=	*c* Gm.
Crucible	=	*a* Gm.
Ash	=	(*c*-*a*) Gm.
HAND BRACE—		
		b Gm.

The following figures giving the analysis of ash from fine filter paper are of interest:

I *Prof. V. Wich:*		II *Professor Brunner:*	
SiO_2	31.876	SiO_2	30.63
Al_2O_3	14.364	Al_2O_3	14.86
Fe_2O_3	9.357	$Fe_2O_3 + P_2O_5$	5.08
P_2O_5	0.238	MnO	1.74
$MnO.Mn_2O_3$	7.637	MgO	7.84
MgO	11.301	CaO	26.28
CaO	21.381	Alkali	13.57
Alkali	2.162		100.00
SO_3	1.684		
	100.000		

The best filter paper is made in Grycksbo, Sweden. In the work of manufacture through a long period of years a practical and effective method of extraction has been employed. Being the most northerly hand-paper mill in the world, there is a long, splendid winter which is favorable for freezing the paper. The water is clear as crystal and practically chemically pure, having its origin in the Dalecarlian mountains. Berzelius, the world renowned chemist, esteemed the Swedish filter paper to be the best in the world, and the mill still maintains its reputation, the paper being in demand over all the old and new world, while the United States takes the bulk of it.

The paper is stamped out in different sizes from 5.5 centimeters to 18.5 centimeters, and is packed in birch bark boxes, which are lined with thin sheets of zinc, hermetically sealed for export to foreign countries.

A good standard of the efficiency of a paper as a filtering medium is represented by the following factors: With a paper having a diameter of six inches, the maximum time for filtration of six cubic inches of water at 90° F. should be 140 seconds, the minimum time, 90 seconds.

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NOTES AND COMMENTS.

Carbide Cakes—Oxygen Metal Cutting.

A specially prepared and treated carbide was shown in London Trades Exhibit. This was compressed by a fully patented process into cylindrical cakes, every particle of carbide being rendered impervious to atmospheric moisture and susceptible to the action of water solely in its liquid state, the generation of gas, therefore, taking place only while water is in actual contact with the cake. Being surrounded by water, the generating plant insures a cool and practically pure gas that is slowly and evenly produced and that is stated to be especially suitable for welding and lighting purposes.

Oxygen metal cutting, together with the necessary apparatus suitable for all classes of engineering work, was exhibited. Pieces of steel were cut through by oxygen flame after the metal had been sufficiently heated by a combined oxyacetylene flame.

Chemical Industries in Europe.

The Bureau of Foreign and Domestic Commerce will soon issue a monograph entitled "Chemical Industries of Belgium, Netherlands, Norway, and Sweden," by Consul Thomas H. Norton, of Chemnitz, Germany, on detail as commercial agent of the Department of Commerce and Labor. The report deals with the supply of raw materials used in the chemical industries, the methods of manufacture, the cost of production, and the foreign and domestic trade of each of the four countries. There are included observations on the state of the chemical-goods trade with the United States and the prospects of improving this trade. Applications will now be listed for copies of the publication.

Steel Belting for Power Transmission.

The use of steel belts in some of the large manufacturing establishments of Huddersfield, England, during the past year has been most satisfactory. At one mill a steel belt 7⅞ ins. wide, weighing 119 lbs., performs the work formerly done by a leather belt 22 ins. wide, weighing 814 lbs., driving 300 H.P. In another mill a steel belt 3½ ins. wide, weighing 12 lbs., does work in driving 40 H.P. that formerly required a leather belt 12 ins. wide, weighing 64 lbs.

These are concrete instances of the success of this German invention. It is especially appreciated in the woolen industry at Huddersfield, where steadiness and uniform speed are essential to the best results. The steel belt is also an economizer of space, does not slip or stretch, and gives the greatest efficiency of power delivery. A government test has shown a saving of 61 H.P. on a drive of 640 H.P. in using the steel belt.

Serviceable wooden pulleys need not be discarded in changing to the metal belts, for the former can be easily, and at small cost, converted into serviceable ones for steel belts by stretching a steel band over the top of the grooves, thus obtaining a flat pulley.

LETTERS TO THE EDITOR.

Potash in Lakes of Western Nebraska.

In the December number of the CHEMICAL ENGINEER reference is made to the potash present in lakes of Western Nebraska. The Jesse Lake mentioned is located two miles from the Burlington railroad, and is twelve miles east of Alliance. Wells dug into the dry lake bed at various times have shown a variation from 11.53 per cent to 19.43 per cent total solids, depending on the climatic conditions at the time of sampling. This strong brine is encountered at a depth of 2 or 3 ft. and extends to a depth of at least 10 ft. The lake water reported in the analysis given by the Mackay School of Mines is evidently surface water from rains, and consequently contains a low percentage of total solids, because of its low gravity staying on the surface and not mixing with the heavier and more concentrated solution in the sand. The lakes are usually dry and the beds are a fine loose sand. A well dug in Jesse Lake 8 ft. square and 8 ft. deep about 200 ft. from shore line flows about 1,000 gals. of strong brine per hour. A ditch across the lake would drain off the salts and furnish brine for a large refinery.

Complete analyses made on several samples of water from this lake show a close uniformity. The following analyses were made on samples taken from shallow wells on the date indicated:

Mar. 21, 1910. North Shore. 16.25%	Total solids in solution. Sept. 25, 1911. East Shore. 16.42%	Nov. 23, 1912. South Shore. 14.17%
Salts in solution showed		
North Shore. 3-21-1910.	East Shore. 9-25-1911.	South Shore. 11-23-1912.
K_2O 28.50%	K_2O 28.34%	K_2O 28.27%
Na_2O 27.64%	Na_2O 27.94%	Na_2O 27.25%
CO_2 ..... 20.17%	CO_2 ..... 21.27%	CO_2 ..... 19.45%
$HCO_2\frac{1}{2}$ .. 7.59%	$HCO_2\frac{1}{2}$ .. 7.31%	$HCO_2\frac{1}{2}$ .. 9.47%
SO_3 ..... 12.09%	SO_3 ..... 11.73%	SO_3 ..... 13.09%
Cl 4.00%	Cl 3.40%	Cl 3.23%
99.99%	99.99%	100.76%

Crystals of potassium sulphate commence to separate out when a 28 per cent total solids is attained.

About twenty other lakes in this vicinity have also been investigated. In general those lakes north of the Burlington railroad show approximately the same analysis as the Jesse Lake, while those south of the railroad are much lower in potash and also sulphates. Of these, the Richardson lake, located about 8 miles south of the Jesse Lake, may be taken as an illustration. This is a lake of approximately 200 acres, and seldom goes dry. Total solids in lake water, 3.75 per cent.

Salts in solution show the following composition:

K_2O	15.02%
Na_2O	40.35%
CO_2	29.42%
$HCO_2\frac{1}{2}$	12.57%
SO_3	.46%
Cl	2.18%
	100.00%

Roughly estimated, the area of the lakes investigated would approximate 5,000 acres. They are located within seven miles of railroad, and it seems highly probable that brine can be pumped to the railroad and refined very cheaply. Experimental work in refining these salts is now under way, and the outlook is very encouraging.

Yours very truly,

John H. Show.

Cudahy Packing Co., South Omaha.

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THE CHEMICAL INDUSTRIES OF BELGIUM.

Investigations of the chemical industries in European countries have been made by U. S. Consul Thomas C. Norton, who was specially detailed for this duty. From his reports the following notes regarding various chemical lines in Belgium are taken:

Sulphuric Acid.—There are 57 factories in Belgium engaged in the manufacture of sulphuric acid or employing it as an important raw material. The chief products in the latter are other minerals, various sulphates, and especially superphosphates. They possess a total motive power of over 6,000 horsepower and employ about 5,000 workmen. Two employ over 400 workmen, and only one uses more than 500 horsepower. The average wage is 60 cents per day, a rate materially below that prevailing in Germany. The maximum wage for skilled labor rarely exceeds $1 per day. As a rule, works are so located that raw material can be furnished by water. Some are placed alongside zinc works, to which they supply roasted ore; others adjoin the great glass works, which depend upon them for sodium sulphate. A number of establishments are so located that they can easily secure coal from the German mines, which costs 20 to 40 cents less than the Belgian coal.

Of the above-mentioned category of chemical works, 26 factories are direct producers of sulphuric acid. In 16 of these the production of superphosphates is a prominent feature. The total volume of lead chambers in use is about 400,000 cubic meters. The annual production of acid is much less than the theoretical capacity of the works. It varies from 300,000 to 320,000 tons of acid, averaging 60 deg. Baumé.

The transportation of sulphuric acid in Belgium, apart from the use of the carboy, is usually effected in iron reservoir cars holding 10 to 15 tons. Some use is made of cars fitted with containers of standstone, eight to the car. Barges with four to six cylindrical iron reservoirs, each holding 25 tons, are employed for shipment by water. Iron cylinders holding 100 to 300 liters (liter equals 1.056 quarts) are employed, usually when the acid is shipped to foreign countries. When shipment is made in iron containers the acid is over 50 deg. Baumé.

The export of sulphuric acid is chiefly to Germany, the total for 1911 being 89,000 tons; Belgium is, in fact, the only country shipping large amounts of sulphuric acid to Germany. As freights are not high, the competition frequently causes very low rates for acid along the Rhine and in Westphalia. Of the total production about two-thirds is required in the manufacture of superphosphate. The other domestic industries consuming important amounts are the manufacture of hydrochloric acid, sodium sulphate, nitric acid, the various metallic sulphates, glucose, nitroglycerin, the saponification of fats and the refining of rapeseed oil.

Nitric Acid—Hydrochloric Acid and Sodium Sulphate.—There are 13 factories engaged in the manufacture of nitric acid. In most cases the bulk of the product is used in the factory itself in connection with other operations. The Valentiner method of distilling under a partial vacuum, with air dilution, is mostly used, although condensation by the Sgoklund and the Guttmann-Rohrmann systems is also encountered. Belgian factories are dependent upon German, and especially upon English, manufactures of acid-proof, air-tight apparatus of stoneware for the needs of this branch.

Most of the nitric acid produced is of 36° strength. A certain amount of 45° and of 48° is prepared for use in the manufacture of artificial silk and high explosives. The annual production, calculated to acid of 36°, is over 11,000 tons. There is an export of about 2,000 tons to the adjacent countries, chiefly to France and the Netherlands. A large fraction of the production is utilized in the domestic manufacture of sulphuric acid.

There are 11 factories that produce annually about 30,000 tons of sulphate and nearly as much hydrochloric acid. Rock salt, brought from Germany, is the usual raw material. Most of the sulphate is consumed in the great glass works of Belgium. The domestic supply is now insufficient to meet the increased demands of the glass industry, and there is an annual import of sulphate exceeding 50,000 tons. It is furnished chiefly by Germany, but France and Great Britain also contribute. The acid is employed in the cementation of copper and in the manufacture of zinc chloride and acetic acid. In the chemical works at Droogenbosch the acid vapors given off from the sulphate oven are used directly for the production of chlorine by the Deacon process. The acid is shipped in

bulk on cars provided with reservoirs of iron, lined with ebonite, which have taken the place of the wooden vats coated with tar formerly in vogue. There is a very limited export of either sulphate or acid.

The production of these two chemicals, as well as the manufacture of sulphuric acid, in Belgium, is controlled by the well organized syndicate, the Union Commerciale, which rigidly restricts production, dividing it equitably among the various works; it thus prevents overproduction and keeps up prices. This syndicate was founded in 1890, and has prevented any serious crises in the sulphuric acid industries.

Superphosphate.—The manufacture of superphosphate has been highly developed in Belgium, partly on account of the abundant supply of cheap sulphuric acid, partly in response to the exceptionally large demands for fertilizers brought about by the intensive agricultural methods of the land. There are 33 superphosphate factories—of these, 16 manufacture their own acid. The industry centers largely about Antwerp, on account of the ease with which raw material can be procured and shipments to other countries effected.

Belgium has fairly extensive deposits of phosphate rock, but they are mostly of an inferior grade. The rock found around Liege and Mons contains 50 per cent or less of tricalcium phosphate. Richer deposits, averaging 60 per cent, are encountered in the vicinity of Baudour. As it is impossible to secure with the domestic rock superphosphate containing much over 15 per cent of P_2O_5, the practice is to mix Belgian phosphates with the purer and richer material imported from other countries. Some is imported from the region of Somme in France. Larger amounts come from Algiers and Tunis and also from the islands of the Pacific. About 65,000 tons of Florida phosphate are imported annually. There is also a small import from the island of Arruba, in the West Indies. These foreign phosphates cost $9.60 to $11.60 per ton, while the native rock ranges from $4.80 to $5.80.

Guano and Thomas Meal.—The treatment of raw guano with sulphuric acid is carried on extensively at Burght, where a large factory is devoted to the production of soluble guano. The imports of crude guano in 1910 were 15,300 tons from Peru and 3,000 tons from the west coast of Africa. Much of the soluble guano is exported to Germany and the Netherlands. A single factory is devoted to the manufacture of artificial guano. The raw material used is leather waste and the refuse from fish-preserving works.

Belgium was one of the first countries to recognize the fertilizing value of Thomas slag. The manufacture of ground slag has assumed large proportions, and Belgium has become a leading exporter of this important product.

The grinding is performed almost exclusively in mills equipped with steel balls, similar to those in general use for cement grinding. The long horizontal, cylindrical mills, which originated in Denmark, render especially good service. Mills are tightly inclosed and ventilators carry off the dust to suitable chambers. The standard of fineness requires a product of which 75 per cent can pass through a sieve with a mesh of 0.17 millimeter (0.0067 inch).

There are seven steel works in the country using the basic process. In addition to the slag which they furnish there is an annual import of about 100,000 tons of crude slag, nine-tenths of which comes from French works. Slag is ground in five steel works and in six other establishments devoted to the manufacture of fertilizers. The preparation of Thomas meal occupies 300 workmen and requires a total of 2,000 h. p. The domestic consumption is not much below 100,000 tons. In 1910 the export attained 521,500 tons, with an average value of $8.59 per metric ton.

The Soda Industry.—The most interesting feature connected with the development of technical chemistry in Belgium is the fact that it is the birthplace of the ammonia-soda process. The fundamental principle of this remarkable process was outlined in England as far back as 1838. Repeated attempts were made for a quarter of a century in England, France and Germany to build up a successful industry, but in vain. Finally, in 1863, Ernest Solvay took up the problem. In his factory, at Couillet, near Charleroi, he successfully perfected the various steps of the process, and shortly placed it on a remunerative basis. By 1873 the time-honored Leblanc soda method of producing soda was seriously threatened, and branch factories for ammonia soda were established in various countries. Ten years later it was recognized on all sides as successful. Since then no Leblanc plants have been constructed, and the existing works are gradually being dismantled. Out of a total annual production for the world of over 2,000,000 tons of soda, it is estimated that only 100,000 tons are produced by the old method. Solvay's success was due to the invention of apparatus admirably adapted for the new class of reactions when operated on a large scale, and to a remarkable co-ordination of all phases of the manufacture, involving a relatively insignificant loss of ammonia.

Organization of the Solvay Co.—Ammonia soda can be manufactured most advantageously where saturated salt springs are available. This fact has prevented Belgium from becoming as great a center of the soda industry as otherwise would be the case. Its supply of salt for this purpose comes from France. The Solvay Company has, in consequence, extended its operations to other lands, and it now constitutes the most powerful international manufacturing organization in the whole domain of chemical industry. The original establishment at Couillet has not been materially enlarged, except to provide for the electrolytic manufacture of chlorine and caustic soda. It now employs 520 workmen. In France the company controls the large works at Dombasle and Salin-de-Giraud, employing

2,500 operatives and manufacturing over 150,000 tons of soda, nearly enough to supply the domestic demand. The English branch, Brunner, Mond & Co., employs over 4,000 operatives in five large works, and produces annually over 200,000 tons of soda, nearly one-half of the total English output. In five German factories, utilizing 21,000 horsepower and employing 5,000 workmen, the company manufactures over one-half of the soda required in the empire. The factory at Torrelavega, in Spain, has 600 workmen, and supplies the entire demand of the country. The Russian factories number three, with 2,500 workmen. Those in Austria-Hungary number five. The two American establishments at Syracuse, N. Y., and Delray, Mich., rank among the largest in the world. In addition to the above list of works under the control of the company, there are ammonia-soda factories in Germany, France and the United States employing modified methods, such as the Honigmann process and the Mallet-Boulouvard system.

The Belgian works at Couillet are regarded as model chemical factories. The eight-hour workday has been introduced, and in diversified provision for the comfort and welfare of employes they compare favorably with the best examples in Germany.

Sal Soda—Sodium Bicarbonate—Caustic Soda.—The domestic demand for bicarbonate is met chiefly by the Solvay works. Sal soda, however, is produced by over twenty small factories. In addition to pure soda crystals, there is an extensive manufacture of a mixed salt containing more or less sulphate, and several factories, in addition, prepare Glauber's salt. The annual output of all these different salts is estimated at 40,000 tons.

There is an annual production of about 2,000 tons of solid caustic. Some small factories still prepare caustic soda from soda ash, with the aid of lime, but most of the above quantity is supplied by the Solvay Company, which has a separate factory at Jemeppe for the electrolytic preparation. The company owns the patents of Castner and Kellner for Europe, and not only employs their methods in their various subsidiary establishments, but also issues licenses to a number of chemical firms scattered over the Continent. At the Jemeppe works the Castner-Kellner method is somewhat modified. In place of double and triple cells, with a salt solution in the cathode compartments, use is made of large single cells containing salt solution alone. A current of mercury enters slowly on one side of the cell, while a layer of sodium amalgam (0.2 per cent Na) flows off on the other side. The salt solution moves in the opposite direction. Decomposition of the amalgam by the aid of steam, with formation of caustic soda, takes place in a separate vessel after it has been conducted back to the cell. This Solvay modification requires a higher electric tension than is needed for the operation of a Castner-Kellner cell, but the construction and operation are much simpler. Solutions containing over 20 per cent of NaOH are easily obtained.

Bleaching Powder.—The chlorine liberated in the electrolytic process at Jemeppe and that obtained by the Deacon method at Droognbusch is used exclusively in the manufacture of bleaching powder. The annual production exceeds 6,000 tons and meets domestic needs. Two factories prepare solutions of bleaching powder, furnishing annually about 1,600 tons. In five factories sodium hypochlorite is made, the output being about 500 tons annually.

Sodium Sulphide and Sulphites—Magnesium Sulphate.—There is an annual production of about 150 tons of the impure sulphide obtained by fusing sulphur and soda. The product is exported chiefly to Argentine, where it is used as a sheep wash.

Sodium bisulphite in solution is manufactured to the extent of 2,500 tons annually. Most of this is exported and destined for use in washing raw wool. There is also a production of about 800 tons of calcium-bisulphite solution. This, as well as sulphurous acid in solution, is used in the country itself for the cleansing of beer casks and for dissolving gelatine. Sulphur dioxide is obtained by burning Italian sulphur.

Saltpeter—Salt—Sulphur.—Five factories in Belgium are engaged in the conversion of sodium nitrate from Chile, with the aid of potassium chloride from Stassfurt, into saltpeter. Three of these factories are connected with the German syndicate for controlling the production of this salt. The annual production is about 2,500 tons. One-third is exported to the Orient and South America. The consumption of saltpeter is steadily declining with the more and more limited use of black gunpowder.

Alumina and Aluminum Sulphate.—The Société Anonyme D'Aluminium, at Selzaete, has introduced into Belgium the Peniakoff process for treating bauxite, and manufactures on an extensive scale alumina, aluminum hydrate, sodium aluminate and various salts of aluminum, especially the sulphate, as well as metallic aluminum. The firm employs 600 operatives and uses 70,000 tons of raw material annually. Bauxite comes from the Var deposits in France. The characteristic feature of the Peniakoff process is the use of sodium sulphate instead of carbonate for transforming the mineral into soluble sodium aluminate. A distinct economy in cost of production is claimed for this method, and an excellent grade of hydrate is produced. The residual solution, after the precipitation of aluminum hydrate with a current carbon dioxide and filtration, is used to prepare caustic and sal soda. Peniakoff has introduced into paper mills the use of a mixture of sodium aluminate and resin, instead of aluminum sulphate and resin soap, for the sizing operation. After this addition has been thoroughly incorporated, sulphuric acid is added to bring about the formation of the sulphate.

Alum—Phosphorus and Phosphoric Acid.—The manufacture of potash alum, apart from its production

in connection with aluminum sulphate, as noted above, is carried on in two factories. In one, at Ampsin, the local aluniferous schists are employed as raw material. The other, at Ruysbrock, uses alunite imported from Tolfa, Italy. The annual production reaches 1,800 tons, and nearly all is exported. These factories find competition with English works increasingly difficult, and they have to contend with the growing tendency to employ aluminum sulphate as a mordant.

Pigments.—The manufacture of white lead is well developed and centers about Courtrai. Of the 7 factories the largest, at Anderlecht, has a productive capacity equaling that of all its rivals combined. The industry occupies 400 workmen and utilizes 440 horsepower. The daily wage ranges from 50 to 70 cents. Much work is done by the piece. The Dutch method of manufacture is in general use. At Anderlecht a single carbonating compartment receives a charge of 35 tons of lead. There is a general use of modern equipment for preventing the respiration of particles of lead compounds by operatives at the different stages of manufacture. A large proportion of the product is ground with oil before entering into commerce. Very rigid regulations were issued in Belgium in 1910 with regard to the sale or transport of white lead in the dry form. Those using it in this condition must be especially licensed, and no one without a license is permitted to purchase the article. The annual product is about 15,000 tons, of which about one-half is exported. Canada and Argentina are important purchasers. The factories in question produce also about 1,500 tons of red lead, of which one-half is exported to France, and a smaller amount of litharge for domestic use.

A large factory near Louvain manufactures annually about 16,000 tons of lithopone, using German heavy spar and residues from the zinc works. About one-half of the output is exported, largely to Great Britain, Spain and the United States.

There are 3 factories occupied with the manufacture of ultramarine, giving occupation to 200 workmen and utilizing 310 horsepower. Use is made of German infusorial earth and English kaolin. Most of the soda required is also imported, as Leblanc soda is preferred in the Belgian works. About two-thirds of the annual production of 2,000 tons finds a foreign market. Competition is keen between Belgian and German manufacturers of ultramarine.

There are 11 establishments devoted to the production of ochers, rouge, etc. Most of the raw material is found in local deposits between Liege and Namur and near Spa. A certain amount of ore is also brought from Spain and Sweden. About 600 tons of rouge and colcothar are manufactured annually from ferrous sulphate. The production of ochers and similar iron pigments reaches 6,000 tons. The bulk of these pigments is exported. There are also some 5 factories that manufacture chrome colors, Schweinfurth green and similar pigments, with an annual export of 1,200 tons.

White Arsenic—Zinc Chloride—Hydrogen Peroxide.—Two factories connected with lead works are engaged in the production of arsenic trioxide from the residues obtained in treating lead ores. The annual output of 2,500 tons is sent for the most part to Germany (460 tons in 1911), Great Britain and the United States.

There is a limited production of about 300 tons of zinc chloride annually in connection with the manufacture of zinc white.

The production of hydrogen peroxide is effected in a factory at Ghent by the direct union of hydrogen and oxygen, according to the recent process of A. Hemptinne. A mixture of the two gases, containing 4 per cent of oxygen, yields the peroxide in large amount when exposed to the action of the electric current. The process is one of promise on account of its simplicity as compared with the prevalent methods based upon the use of the peroxides of barium or sodium. It is to be noted, however, in this connection that German chemists are steadily perfecting processes for securing hydrogen peroxide by the continued electrolysis of sulphuric acid after its transformation into persulphuric acid, and also by the use of solid persulphates and of perborates.

Ammonia and Ammonium Sulphate.—In several gas works the Solvay method for securing pure ammonia water is used, and the operations are carried on under the direction of the Solvay company with its special apparatus. The larger gas works manufacture ammonium sulphate directly. The annual output of sulphate from gas works exceeds 4,000 tons. From coke ovens there is an additional quantity of 10,700 tons, making a total of 14,700 tons. This does not suffice to meet the demands of domestic agriculture, and there is a net import of 2,500 tons from Germany. The Belgian coke works are now tending to an increased production of sulphate by the direct method, the oven gases being in part brought immediately in contact with sulphuric acid.

Belgian Tar Works—Aniline Dyes.—The six tar works in Belgium are well equipped and handle annually over 100,000 tons. A little less than half of this comes from abroad, chiefly from cities on the coast of the Baltic, the Atlantic and even the Mediterranean. An additional factory is devoted to the refining of naphthalene and of anthracene. The annual output is as follows, in metric tons: Benzine, toluene, etc., 4,800; carbolic acid, 250; naphthalene, crude, 9,000; heavy oils, 22,000; anthracene (35 per cent), 4,500; pitch, 62,000.

About two-thirds of the naphthalene is refined. A large share of the anthracene is also refined to the 80 per cent grade. All of these products except pitch are exported in quantity. Much of the creosote oil goes to France. The United States purchases about 1,000 tons annually of naphthalene. Pitch is imported in large amounts, Germany furnishing 38,000 tons. Its chief use is for manufacturing briquets of coal

dust. The Societe Anonyme des Aggiomeres Reunis du Bassin de Charleroi, with works at Marcinelle and Chatelinan, is the leading firm in the Belgian tar industry, in which over 600 workmen are engaged.

Little effort is made in Belgium to manufacture coal tar colors and compete with the great works of France and Germany. Two small factories make quinoline yellow, various nigrosines, soluble blues, etc. The largest of these, at Hoeren, employs over 100 operatives, and exports annually in excess of 500 tons. The great mass of dye-stuffs comes from Germany. In 1911 the purchases were: Anilin dyes in general, 2,000 tons; alizarin, 92 tons. The annual consumption of German synthetic indigo is 700 tons. Belgium conducts a large trade in dyes and coloring material, apart from her own important production of mineral pigments. In 1910 the total imports of colors and pigments, excluding indigo, amounted to $6,800,000, and the exports to $11,406,000. The sales of German indigo reached 4,665 tons, of which nearly all was taken by China.

Oils and Fats.—The country consumed in 1910 150,000 tons of refined petroleum, of which 60 per cent came from the United States. The remainder was contributed by Roumania, Galicia, and the Caucasus. There is 1 petroleum refinery in Belgium, but the business of refining has largely ceased, and the import of crude petroleum is insignificant. Two factories handle heavy oils and 4 make a specialty of mineral lubricating oils. The annual product is 10,000 tons, of which 70 per cent is exported. A considerable amount of vaseline also is isolated in these works.

Animal fats are employed chiefly in the production of oleomargarine and margarine. Their import reaches 2,000 tons. There is likewise a net import of oleomargarine and similar products amounting to 1,300 tons.

About 5,000 tons of resin are distilled annually in some 10 establishments. The product of nearly 4,000 tons is exported largely for use as a lubricant. Most of the resin comes from the United States. A small portion is contributed by France.

Vegetable Oils.—The manufacture of vegetable oils is very important, as there are no less than 160 oil mills. Belgium itself furnishes a large amount of linseed and rapeseed, but the bulk of the oleaginous seeds is imported. In 1910 the net imports were as follows, in metric tons: Castor oil bean, 10,240; cottonseed, 990; linseed, 70,600; peanuts, 8,100; poppy seed, 3,800; rapeseed, 47,000; sesame, 1,600; divers, 32,000; copra, 19,700; palm nuts, 7,400.

Rapeseed oil is manufactured in 30 mills, several of which refine crude imported oil. The annual output exceeds 20,000 tons. Some is exported, chiefly to Great Britain. The demand for this oil as an illuminant in mines is steadily increasing.

Margarine—Candles—Soap.—The production of margarine and other artificial butters has become an important industry of late years. There are now 16 factories, of which three are devoted to the manufacture of oleomargarine. In 1910 the 13 other factories produced 10,074 tons, of which 9,583 tons were classified strictly as margarine. The materials used were as follows, in metric tons: Oleomargarine, 3,071; other fats, 1,641; pure butter, 50; milk, 5,325; cottonseed oil, 2,648; peanut oil, 181; sesame oil, 501; other oil, 536. There was a small export of 533 tons and an import of 13 tons.

The stearine industry of Belgium has reached a high state of perfection, and its products are well known in most countries. There are 4 factories. The most important, the Manufacture Royale, at Brussels, employs 380 operatives and uses 10,000 tons of raw material annually. The output includes 5,000 tons of stearin, 2,000 tons of candles, 3,000 tons of oleine and 400 tons of glycerin. Glycerin is refined here and in the other works, a certain amount of crude glycerin, also, being imported for the purpose. Belgium exports about 70 per cent of the total output of candles. In 1910 the shipments reached 4,250 tons. Argentine, India and Turkey were the chief purchasers, but sales were made to nearly every country. There is an annual import of 7,000 tons of stearin, 2,500 tons of oleine and 800 tons of refined glycerin.

The soap industry is relatively less developed. There are 12 factories producing hard soaps, and there is an increasing variety of toilet soaps. The total annual output is estimated at 5,000 tons. In 4 other establishments soap powder is produced to the extent of 2,000 tons. Soft soap is made in a number of small works. Domestic consumption is, however, in excess of the supply. In 1910 there were net imports of 407 tons of toilet soap—chiefly from Great Britain, Germany and France—143 tons of other hard soap and 60 tons of soft soap.

Varnishes—Perfumes—Pharmaceutical Products.—There is a moderate production of varnish, chiefly by firms engaged in the manufacture of lubricants or of colors. It is thus far inadequate for domestic needs, and in 1910 net imports reached 933 tons, with an average value per ton of $347. Great Britain supplies about one-half of the imports; the remainder comes from France, Holland, Germany and the United States. The value of the imports from America was $40,000.

The manufacture of perfumes and cosmetics is still in its infancy in Belgium, although much is done to meet the domestic demand. As in the case of toilet soaps there is a large import, two-thirds of which is supplied by France. This import in 1910 reached 312 tons, with a value of $463,000. There was a small export of 21 tons.

There are five establishments in Belgium engaged in the manufacture of pharmaceutical products and pure chemicals. Their operatives number 150. Thus far they furnish only a small part of the domestic consumption.

ACCURACY AND LIMITATIONS OF COAL ANALYSIS.

By A. C. FIELDNER.*

In recent years chemical and physical tests have come into use in connection with the mining and utilization of coal. Within certain limits these tests are useful not only in establishing the fuel value but in directing the coal into the proper market for which it is best adapted, and of maintaining the standard of the output to meet the requirements of this market. The growing practice of buying on specifications demands accuracy and strict uniformity in the methods of sampling and analysis. Chemists who make only occasional analyses of coal do not as a rule realize the empirical nature of the proximate analysis, and while they may obtain concordant results as far as their own laboratories are concerned, their results may not agree with those obtained in another laboratory. These discrepancies, which are more likely to occur in some determinations like that of volatile matter or of fixed carbon, tend to discredit the whole analysis in the eyes of engineers not familiar with the difficulties peculiar to each individual determination. The object of this paper is to call attention to the fact that some constituents may be determined much more accurately than others, and to present some experimental data bearing on the probable variations that may occur in good laboratory practice.

NATURE OF COAL.

Coal is used principally for fuel purposes; hence its value, other things being equal, is proportional to its calorific power. The different kinds of coal, however, vary greatly in character, so much so that each has its own particular field of usefulness. For instance, a Pittsburgh steam coal cannot be burned efficiently in an anthracite furnace, nor can a coal high in sulphur or phosphorus be used for the manufacture of foundry coke. Certain other tests, then, are also required, and for this purpose we have the conventional proximate analysis and sulphur or phosphorus determinations. While these tests may be sufficient for most industrial purposes, it is desirable at times to know the elementary composition of the coal as shown in an ultimate analysis, and its clinkering properties as indicated in the relative fusibility of the ash. No doubt other tests more suitable for individual purposes will come into use as the chemist learns what coal really is.

It is generally conceded by geologists that coal has its origin in vegetable matter that was accumulated and buried in past geological ages. Several different theories have been advanced as to the exact manner of accumulation and the particular kinds of vegetation or vegetable products that were involved. At any rate, this accumulation became more or less altered and concentrated under swampy conditions and finally buried under a load of sediments, to be subjected to a further change by the action of heat and pressure. In more or less intimate mixture with these organic remains was deposited silt, sand, clay, and other earthy materials. Sometimes layers of sediments were laid down between the coal-forming vegetation. It is not surprising, then, that the present chemical constitution of coal is not only of an extremely complex nature but that it varies from one bed to another.

For fuel purposes the constituents of coal may be grouped into the following three classes:

1. Water or moisture.
2. The mineral impurities which remain in a somewhat altered condition, as ash on burning the coal.
3. The organic or combustible matter, which like the original vegetable matter, is composed mainly of the elements carbon, hydrogen, oxygen and nitrogen.

MOISTURE.

Moisture may be accurately determined in an inorganic substance like iron ore by drying the material at a temperature slightly above the boiling point of water and noting the loss in weight. The same method when applied to coal is complicated by the oxidizing tendencies of the organic compounds, and the possibility of loss of some water of composition at the temperature of drying. The present methods of analytical chemistry do not distinguish with certainty between added moisture or water that is simply absorbed by the coal particles, and water that may be in some unstable chemical combination in the coal substance. The usual method of drying a pulverized sample for one hour at 105° C. (221° F.) is therefore somewhat arbitrary, and to secure uniform results a strict adherence to a standard method of procedure is necessary.

In the Bureau of Mines method[1] the moisture is determined in two stages: (1) The coarse sample received by the laboratory is pulverized to ¼-in. size and then air-dried at 30°-50° C. (86°-95° F.). The loss in weight, which is called the air-drying loss, includes all the superficial moisture and a large portion of the loosely retained moisture. (2) The air-dried sample is then pulverized in a closed ball mill to avoid loss of moisture, mixed and sampled down to a small, powdered sample in which the residual moisture is determined, by heating 1 gram for 1 hour at 105° C. (221° F.) in an oven through which dry air is being circulated. By this method duplicate results in the same powdered sample seldom vary more than 0.15 per cent.

ASH.

Ash is the incombustible residue left on burning coal. It is derived from the mineral impurities in the coal and is largely composed of silica, alumina, lime, and iron compounds, together with smaller quantities

*By permission of the Director, U. S. Bureau of Mines. Paper read before American Coal Mining Institute, Pittsburgh, Pa., Dec. 19, 1912.

[1]Stanton, F. M., and Fieldner, A. C. Methods of analyzing coal and coke. Technical paper 8, Bureau of Mines.

of magnesia, titanium, and alkali compounds. The silica, alumina and titanium are derived from sand, clay, shale and slate; the iron oxide mainly from iron pyrite; and the lime and magnesia from their corresponding carbonates and sulphates.

The ash-forming constituents of coal may be classified in two groups.

1. Mineral matter present in an intimate mixture with the coal substance, derived either from the vegetable structure or from earthy matter intermixed as silt during the process of coal formation.

2. Mineral matter occurring in the form of thin bands and nodules of shale, bone, and pyrites; in this class are also the fragments of roof and floor that become mixed with the coal in mining.

3. Mineral matter from the first source can not be removed by washing methods; it is sometimes called the "intrinsic ash" of the coal. Mineral matter from the second source, sometimes called "Extraneous ash," may be removed by methods of washing, screening and picking. In the laboratory a similar separation can be made by the float-and-sink test. Coal has a specific gravity somewhat less than 1.35; the impurities are heavier; hence a separation may be made by placing the coal, crushed to a suitable size, in a solution of calcium or zinc chloride of 1.35 specific gravity. The coal will float, while the shale, bone, pyrite, etc., will sink. In this way the possibility of improving the quality of coal by washing can be determined.

The determination of ash, although one of the simplest operations, is also beset with certain difficulties that lead to disagreement among different laboratories, more especially with coals containing notable quantities of calcium carbonate and iron pyrites. On ignition the calcium carbonate is decomposed, and carbon dioxide driven off, either partially or completely, depending on the duration and temperature of ignition. The iron pyrite is changed to ferric oxide, while more or less of the sulphur combines with the lime to form $CaSO_4$. For example, in certain experiments with Illinois coals that contained notable quantities of calcium carbonate and sulphur, 14 per cent ash was obtained by ignition to constant weight at a low-red heat, and 13 per cent ash was obtained by ignition at a bright-red heat. To secure concordant results a standard temperature should be adopted. If this is done, duplicate determinations on the same powdered sample will agree to within 0.2 per cent.

Coal ash as determined usually weighs less than the mineral matter from which it is produced. This is due mainly to the loss during ignition of volatile constituents; the shale and clay will lose their water of composition; the carbonates will be more or less decomposed, giving off carbon dioxide; and the iron pyrites will be changed to ferric oxide, giving off sulphur.

Several methods have been proposed to compute the weight of original mineral matter in the coal, by adding correction to the weight of ash obtained by ignition. These methods are, however, too complicated and uncertain in their general application to all classes of coal to be used in technical work.

VOLATILE MATTER AND FIXED CARBON.

The volatile matter and fixed carbon represent the relative proportions of gaseous and solid combustible matter that may be obtained from the coal by heating it in a closed vessel. This is done by heating a finely powdered sample in a small, covered platinum crucible, in the flame of a bunsen or Meker burner, for exactly seven minutes. The volatile matter consists mainly of the combustible gases—hydrogen, carbon monoxide, methane, and other hydrocarbons—and some non-combustible gases as carbon dioxide and water vapor. The volatile matter does not include water present in the coal as moisture at 105° C. (221° F.).

The residue of coke left in the crucible after deducting the ash is reported as "fixed carbon." The fixed carbon does not represent the total carbon in the coal, as a portion of this element is driven out in combination with hydrogen in the volatile matter; furthermore, fixed carbon is not pure carbon, but still contains several tenths per cent each of carbon, hydrogen, and oxygen; from 0.4 to 1.0 per cent nitrogen; and about half the sulphur that was in the coal. It should be clearly understood that the terms "volatile matter" or "volatile combustible matter" and "fixed carbon" do not represent any definite compounds which existed in the coal before heating. The method of determination is purely arbitrary, and variations in temperature and rate of heating will cause variations amounting to several per cent; even with a strict adherence to the method recommended by the American Chemical Society, variations of three and four per cent in both the volatile matter and fixed carbon may occur in different laboratories. One of the most prominent factors in causing variations is the temperature at which the crucible is heated. This is especially pronounced in anthracite and semi-bituminous coal. It is not improbable for one laboratory to report 4 per cent and another 7 per cent volatile matter on the same sample of anthracite, or 14 per cent and 17 per cent respectively on the same sample of Pocahontas coal. The different percentages of volatile matter were actually produced by different conditions of heat treatment. Caution must therefore be observed in making comparisons of the volatile matter and fixed carbon in proximate analyses made in different laboratories. Even determinations made at the same laboratory by the same analyst may vary to the extent of 0.5 per cent.

Recently a series of experiments were made at the Pittsburgh station of the Bureau of Mines to provide data on which to base a temperature specification at which the most uniform analytical results could be

obtained.[2] A series of determinations at temperatures varying from 750° C. (1,382° F.) to 1,100° C. (2,012° F.) were made on five different types of coal and one sample of foundry coke. These determinations were made in a 30 c. c. platinum crucible, which was heated in an electric furnace under uniform conditions. Oxidation was prevented by passing nitrogen into the crucible. The results obtained are given in Table I, and graphically illustrated in the curves in Figure 1.

TABLE I.—VOLATILE MATTER AT DIFFERENT TEMPERATURES.

Temperatures.	Per cent of volatile matter. Coke.	Anthracite.	Pocahontas.	Pittsburgh.	Colorado.	Illinois.
740- 745	0.40	...	....	32.86	32.99	....
745- 750	...	2.84	14.66	....	....	32.38
		2.96				
750- 755	0.51	...	14.80	33.13	33.00	....
755- 760	0.56	...	....	....	....	32.51
765- 770	...	2.93	....	....	....	....
770- 775	...	...	....	33.68	....	....
785- 790	...	...	....	33.69	....	....
790- 795	...	...	....	....	35.70	....
795- 800	...	3.25	....	33.89	....	....
805- 810	0.55	...	15.88	34.05	34.07	....
	0.54					
810- 815	0.60	3.33	....	34.11	....	33.60
815- 820	...	3.23	....	....	....	....
825- 830	...	...	16.17	....	....	33.98
835- 840	0.63	...	....	....	....	....
840- 845	...	5.57	....	....	....	....
850- 855	...	3.59	....	....	34.12	....
855- 860	0.53	...	....	34.70	....	34.54
860- 865	0.44	...	....	34.75	....	34.63
865- 870	...	3.70	....	....	....	....
870- 875	0.53	...	....	....	....	....
885- 890	...	...	16.49	....	....	....
890- 895	...	...	16.45	....	....	....
895- 900	...	...	....	....	....	34.99
905- 910	...	...	....	34.57	....	....
910- 915	0.68	3.93	....	....	34.62	....
		4.15				
915- 920	...	...	16.70	34.75	34.80	....
			16.92			
920- 925	...	...	....	....	....	35.10
935- 940	0.71	...	....	....	....	....
955- 960	...	...	....	....	34.93	....
960- 965	...	...	17.03	35.00	34.94	35.60
						35.70
965- 970	0.80	...	....	34.92	....	....
970- 975	0.85	...	17.13	....	....	....
975- 980	...	4.63	....	....	....	....
		4.63				
1000-1005	...	...	....	34.87	....	....
1005-1010	0.95	...	17.10	34.82	34.97	....
1010-1015	0.91	4.86	....	....	35.02	35.55
						35.86
1015-1020	...	5.00	....	....	....	....
1025-1030	...	...	17.30	....	....	....
1050-1085	1.02	...	....	....	....	35.63
1055-1060	1.02	...	....	....	....	35.89
1060-1065	...	...	....	....	34.89	....
1065-1070	...	5.19	17.21	34.72	34.97	....
			17.33	34.82		
1075-1080	...	5.36	....	....	....	....
1085-1090	...	...	17.35	....	....	....
1110-1115	...	5.60	17.49	....	....	....
1120-1125	1.22	...	....	....	....	....
1125-1130	...	5.71	....	....	....	....
1130-1135	1.25	...	....	....	....	....

It will be seen that more volatile matter is obtained at the higher temperatures, although the ratio between temperature and volatile matter varies in the different coals tested. The curve for anthracite is remarkable in that it is practically a straight line. The curves for the three bituminous coals become horizontal at about 950° C. (1,742° F.). The Pocahontas curve retains a slight upward inclination even at the higher temperatures.

From the analytical standpoint, 950°-1,000° C. (1,742°-1,832° F.) appears to be the best temperature for the determination of volatile matter, as slight variations in temperature on the upper end of the curve produce less deviation in results.

SULPHUR.

Sulphur is usually determined in connection with the proximate analysis. It is classified with the impurities and undesirable constituents of coal, although it usually exists in a combustible form and contributes to the heating value. Commonly sulphur is present as iron pyrite, either in brassy lumps and bands or in very fine particles uniformly distributed throughout the coal. Sulphur may also occur in combination with iron and lime as sulphates and in combination with the coal substance as organic compounds.

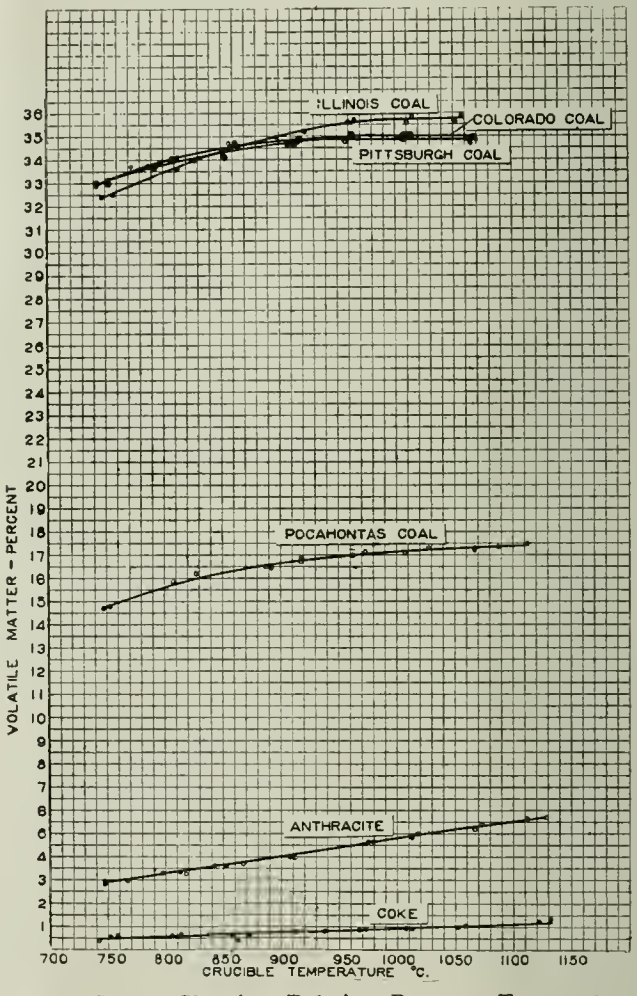


Fig. 1—Curves Showing Relation Between Temperature and Volatile Matter.

Duplicate determinations by the "Eschka" method on the same powdered sample will usually agree to within 0.05 per cent. Where much sulphur is present

[2]Fieldner, A. C., and Hall, A. H. Influence of temperature on the determination of volatile matter in coal. Eighth International Congress of Applied Chemistry, vol. X, p. 139 (1912).

in visible form, as pyrite, difficulty is experienced in obtaining a representative powdered sample from the coarse sample, and somewhat greater errors due to inaccuracies in sampling may occur.

ULTIMATE ANALYSIS.

In an ultimate analysis the organic matter of the coal is resolved into its chemical elements, viz., carbon, hydrogen, oxygen, and nitrogen. These elements, together with the ash, are taken as equal to 100 per cent. As there is no direct method for the determination of oxygen, it is estimated by subtracting the sum of the other five constituents from 100. This method throws the summation of all the errors incurred in the other determinations upon the oxygen.

The determination of carbon, hydrogen, and nitrogen, while requiring experience and a considerable degree of analytical skill on the part of the chemist, is not subject to the arbitrary conditions that must be maintained in the proximate analysis. As the chemist is dealing with definite chemical elements, he should be able to duplicate his determinations within the following limits: Carbon 0.3 per cent, hydrogen 0.05 per cent, nitrogen 0.03 per cent.

It is unfortunate that no direct method has yet been devised for the determination of oxygen. The percentage of oxygen is an important factor in many of the problems connected with the classification, spontaneous combustion, weathering, and inflammability of coal. In the present method of estimation the oxygen percentage is subject to an error equal to the algebraic sum of the individual errors incurred in the determination of carbon, hydrogen, nitrogen, sulphur, and ash. The most serious of these errors is due to the difference in weight between the ash and the mineral matter (exclusive of sulphur, which is separately determined) as it occurs in the coal. For instance, if all the sulphur is present as iron pyrites, the oxygen percentage will have a negative error equal to three-eights of the sulphur. This correction, however, is applicable only when the percentage of pyritic sulphur is known, and a satisfactory method for determining all the different forms of sulphur found in coal is yet to be devised. Furthermore, there are errors in the opposite direction that tend to compensate the error due to the oxidation of iron pyrites, notably the loss of certain mineral constituents like carbon dioxide from carbonates and water of composition from the shaly constituents. Prof. Parr[3] has found the water of composition in Illinois coals to be approximately 8 per cent of the ash. In a coal with 10 per cent ash this would cause an error of —0.71 per cent in the oxygen; if this same coal happened to contain 2 per cent sulphur as iron pyrite, an additional error of +0.75 per cent would be incurred in the oxygen. The two errors would thus compensate to within 0.04 per cent; whether the final oxygen error is positive or negative would depend upon the relative proportions of shale and pyrite in the coal, and upon the quantities of carbonates of iron and lime. It is doubtful if any generally applied method of correction would materially increase the accuracy of the oxygen result.

The ultimate analysis as usually made does not distinguish between the carbon and hydrogen derived from the organic or combustible matter of the coal, and the small proportion of these elements that may be present in an incombustible form in the mineral impurities. Illinois coals, as shown by Prof. Parr[4] often contain 0.1-0.7 per cent carbon as calcium carbonate. Most of the coal in the Appalachian field is comparatively free from carbonates. A small proportion of the hydrogen, usually from a few hundredths to about 0.1 per cent, has its origin in the water of composition of the clay or shaly material. While correction can be made with the aid of special chemical methods, for the small percentages of inorganic carbon, hydrogen, and oxygen, it is not necessary in the ordinary technical analyses.

In the consideration of an ultimate analysis it must be kept in mind that the hydrogen and oxygen of the moisture in the sample are included with the hydrogen and oxygen of the dry coal substance. Usually before making comparisons ultimate analyses are computed to a dry-coal basis, thus giving the relative proportions of hydrogen and oxygen in the dry coal.

The term "available hydrogen" often used in the computation of the calorific value of a coal from the ultimate analysis, is based on the assumption that all the oxygen in the coal is combined with hydrogen in the proper ratio to form water. The amount of hydrogen thus combined and not available for producing heat is equal to one-eighth of the oxygen; the remainder of the hydrogen, or "available hydrogen," is combined with the carbon and contributes to the heating value of the coal. This hypothesis is fairly well supported in the case of anthracite and bituminous coals by the general agreement of calorific values calculated from the ultimate analysis by Dulong's formula with the values determined by the bomb calorimeter.

CALORIFIC VALUE.

The calorific value of a fuel is the total quantity of heat developed by the complete combustion of the unit weight of fuel. In the metric system of measurement which is usually used by chemists and physicists, the heat units are the gram calorie and the kilogram calorie. The gram calorie, or small calorie (cal.), is the amount of heat required to raise the temperature of one gram of water 1° C. at 15° C. and the kilogram calorie, or large calorie (cal.), is the amount of heat required to raise the temperature of one kilogram of water 1° at 15° C.

In the English system which is generally used by engineers, the heat unit is the "British Thermal Unit," or B. t. u. The British Thermal Unit is the quantity of heat required to raise the temperature of one pound

[3]Parr, S. W., Bull. Ill. State Geol. Survey, No. 8, page 154.

[4]Bull. 16, Ill. State Geol. Survey, page 232.

of water, 1° F., at 60° F. Calorific values given in calories per gram, may be converted into British Thermal Units per pound, by multiplying by 1.8, because the temperature rise produced in one gram of water by the heat in one gram of coal, will be the same as the rise produced in one pound of water by the heat in one pound of coal, hence, the relation between the calorific values of one gram and one pound of fuel is simply that of the two different thermometric scales, which is 9 5 .

The most accurate method of determining the total heating value is by combustion in a bomb calorimeter. The instrument should be carefully standardized by burning substances of known calorific value such as the standard samples of cane sugar, naphthalene, and benzoic acid, that are now being furnished by the Bureau of Standards. The standardization should be conducted under exactly the same conditions, and with the same thermometer, that is used in the tests. The use of calibrated thermometers is essential. In carefully conducted calorimetric work the probable error should not exceed 0.5 per cent, which corresponds to about 50 B. t. u. in a high grade coal. This is a higher degree of accuracy than can be obtained in the usual methods of sampling, which oftentimes increase the error to 100 B. t. u.

CALCULATION OF CALORIFIC VALUE BY DULONG'S FORMULA.

Before the bomb calorimeter came into general use, the heating value of a coal was frequently calculated from the ultimate analysis by Dulong's formula:

(1) Calorific value in calories per gram—
8,080 C plus 34,460 $(H—O/8)$ plus 2,250 S.

(2) Calorific value in B. t. u. per pound—
14,544 C plus 62,026 $(H—O/8)$ plus 4,050 S.

In the above formulas, C, H, O and S are the respective proportions of carbon, hydrogen, oxygen and sulphur.

Aside from the fact that an ultimate analysis is more expensive and time consuming than a calorimetric determination, there are the following theoretical objections to be considered:

(1) The heating value of the elements—carbon, hydrogen and sulphur, as given in the formula—have not been established with any great degree of accuracy.

(2) The heating value of an element in the free state and as a component of a chemical compound is not necessarily the same, as a matter of fact it usually varies, due to absorption or evolution of heat in forming the compound.

(3) The usual assumption that from the standpoint of heat development all the oxygen is combined with hydrogen, may not be true: some of the oxygen may be linked with carbon.

(4) The relative accuracy of the calculated results are subject to the uncertainty of the oxygen estimation.

On the other hand, in spite of the objections just cited, there is fairly close agreement between the calorific values calculated by Dulong's formula and those determined by the calorimeter. Lord and Somermeier[5] in a large series of analyses of the coals of Ohio found that with very few exceptions the results obtained by Dulong's formula were with 1-1½ per cent of the values obtained with the bomb calorimeter. This degree of accuracy has also been found to hold true with anthracite, semi-bituminous and bituminous coals of various parts of the United States as shown in Table II:

[5] Geological Survey of Ohio, 4th series, Bull. 9 (1908), page 267.

TABLE II.—A COMPARISON OF CALORIFIC VALUES AS DETERMINED IN THE BOMB CALORIMETER AND AS CALCULATED FROM THE ULTIMATE ANALYSIS BY DULONG'S FORMULA.
Colarific value in B. t. u. per pound = 14,544 C plus 62,028 (H— O/8) plus 40,505:

Description.		Proximate analysis as received.			Calorific value as received.			Error in calculated calorific value.
Sub-bituminous Coal, Rocky Mountain field—	Lab. No.	Moisture. Per cent.	Ash. Per cent.	Volatile matter. Per cent.	Determined. B. t. u.	Calculated. B. t. u.	Difference. B. t. u.	Per cent.
Colorado.								
El Paso County	10732	31.1	13.9	26.0	6199	6237	38	.6
El Paso County	12099	26.2	6.5	29.7	6552	8114	—238	—2.8
El Paso County	10741	33.7	18.2	23.5	5506	5542	36	.7
Wyoming.								
Converse County	11048	28.1	4.6	31.6	8350	8057	—295	—3.5
Converse County	10775	27.7	10.0	26.7	7808	7763	— 45	—.6
Converse County	10740	27.9	8.3	27.1	7927	8001	74	.9
Fremont County	10843	20.9	3.7	32.0	9781	9673	—108	—1.1
Fremont County	10842	21.1	5.8	31.4	9463	9293	—170	—1.8
Johnson County	11059	16.8	15.0	31.4	8480	8440	— 40	—.5
Johnson County	10827	23.5	5.2	35.6	9050	8719	—331	—3.8
Sheridan County	10810	22.7	3.4	32.2	9344	9221	—123	—1.3
Sheridan County	10811	24.7	3.7	31.8	9007	8852	—155	—1.7
Sheridan County	10825	22.6	4.6	32.5	9218	9131	—187	—2.0
Sheridan County	10826	22.1	4.4	33.4	9256	8978	—275	—3.0
Sheridan County	10822	23.5	4.9	31.2	9121	8935	—186	—2.0
Sheridan County	12005	22.3	3.7	35.0	9617	9364	—253	—2.6
Sheridan County	12008	23.1	3.2	31.9	9494	9302	—182	—1.9
Sheridan County	12006	23.4	3.6	33.6	9392	9259	—133	—1.4
Sweetwater County	11510	16.3	2.1	34.9	11153	11066	— 67	— .6
Sweetwater County	11460	13.1	3.4	35.8	11619	11576	— 43	— .4

Mean algebraic error in 20 samples	—1.4
Maximum negative error	3.8
Maximum positive error	.9

Description.		Proximate analysis dry basis.			Calorific value dry basis.			Error in calculated calorific value.
Dry Peat—	Lab. No.	Moisture. Per cent.	Ash. Per cent.	Volatile matter. Per cent.	Determined. B. t. u.	Calculated. B. t. u.	Difference. B. t. u.	Per cent.
Massachusetts	12767	...	20.1	56.3	7745	7452	—293	—3.8
Massachusetts	12766	...	11.2	64.2	9018	8477	—541	—6.0
Massachusetts	10834	...	4.0	65.6	10285	9629	—656	—6.4
Massachusetts	10833	...	4.0	64.4	10305	9712	—587	—5.7
Maine	5978	...	5.2	70.0	8471	7542	—929	—11.0
Maine	5983	...	3.8	67.6	9598	8600	—998	—10.4
Maine	5994	...	6.7	70.3	8132	7319	—813	—10.0
Maine	5975	...	3.8	66.6	8915	7974	—941	—10.6
Michigan	6720	...	14.1	57.5	9139	8423	—716	—7.9
Wisconsin	6280	...	17.3	58.0	8149	7489	—660	—8.1
Wisconsin	6507	...	18.7	55.8	7835	7606	—229	—2.9
Wisconsin	6290	...	26.2	59.2	7465	7002	—463	—6.2

Mean algebraic error in 12 samples..... 7.4
Maximum error 11.0

Description.		Proximate analysis as received.			Calorific value as received.			Error in calculated calorific value.
Lignite—	Lab. No.	Moisture. Per cent.	Ash. Per cent.	Volatile matter. Per cent.	Determined. B. t. u.	Calculated. B. t. u.	Difference. B. t. u.	Per cent.
Valley Co., Montana	10898	42.8	4.6	25.7	6105	5785	—320	—5.2
Valley Co., Montana	10899	41.3	4.8	25.7	6260	5974	—286	—4.6
Valley Co., Montana	10900	41.6	4.1	27.1	5733	5467	—266	—4.7
Valley Co., Montana	10725	38.9	6.2	27.2	6014	5843	—171	—2.8
Valley Co., Montana	10726	35.3	7.7	31.8	5404	5227	—177	—3.3
Valley Co., Montana	10727	37.5	6.1	26.8	6580	6408	—172	—2.6
Valley Co., Montana	10724	32.6	9.1	27.4	6712	6664	—48	—.7
Valley Co., Montana	11002	40.4	7.5	24.5	5830	5598	—232	—4.0
Valley Co., Montana	11003	39.3	5.7	24.2	6278	6059	—219	—3.5
Valley Co., Montana	11004	37.7	5.5	25.8	6700	6550	—150	—2.3
Valley Co., Montana	11006	41.6	5.6	26.7	5278	4991	—287	—5.4
Valley Co., Montana	11005	40.7	6.2	25.2	6147	5980	—167	—2.7
Morton Co., N. D.	14729	36.2	8.7	29.8	6700	6559	—141	—2.1
Morton Co., N. D.	1416	36.8	5.1	28.2	7204	6928	—276	—3.9
Perkins Co., S. D.	12488	42.5	9.0	23.2	5954	5913	—41	—.7
Perkins Co., S. D.	12453	39.2	8.4	24.7	6307	6277	—30	—.5
Texas	1456	34.7	11.2	32.2	7056	6849	—207	—2.9
Texas	1597	33.7	7.3	24.3	7348	7155	—193	—2.6
Texas	2717	33.9	7.3	27.5	7497	7204	—293	—3.9

Mean algebraic error in 19 samples.....—3.1
Maximum error in 19 samples.....—5.4

Description.		Proximate analysis as received.			Calorific value as received.			Error in calculated calorific value.
Bituminous coal, Rocky Mountain field—	Lab. No.	Moisture. Per cent.	Ash. Per cent.	Volatile matter. Per cent.	Determined. B. t. u.	Calculated. B. t. u.	Difference. B. t. u.	Per cent.
Canada.								
Alberta	14883	10.6	16.7	36.4	9819	9828	9	.1
Alberta	14882	9.8	6.8	40.2	11412	11385	— 27	—.2
Alberta	13177	6.5	16.2	34.5	10737	10582	—155	—1.4
Alberta	12737	2.0	17.6	27.4	12208	12166	— 42	— .4
Colorado.								
La Plata County	14775	7.1	5.9	38.1	12672	12649	— 23	— .2
La Plata County	14772	3.0	6.9	34.8	13714	13853	139	1.0
Fremont County	13395	10.3	5.5	38.3	11416	11230	—186	—1.6
Las Animas County	13364	3.3	15.6	52.0	12357	12175	—182	—1.1
Las Animas County	13254	5.4	8.6	33.0	13237	13176	— 61	— .5
Las Animas County	13253	6.3	14.1	30.2	12145	12121	— 24	— .2
New Mexico.								
Colfax County	13367	5.7	13.2	35.8	12019	12015	— 4	0
Colfax County	12235	3.3	12.3	35.7	12757	12773	16	.1
Colfax County	12338	3.6	12.0	36.1	12623	12580	— 43	— .3
Utah.								
Carbon County	10906	7.5	5.6	39.7	12521	12523	2	0
Carbon County	10909	5.7	7.0	40.8	12647	12605	— 42	— .3
Oregon	12825	3.3	7.2	40.3	12640	12597	— 43	— .3
Oregon	12824	2.5	8.6	37.3	13039	13070	— 31	— .2
Washington.								
Kittits County	11525	3.9	12.6	37.0	12434	12546	112	.9
Kittits County	11526	3.8	11.5	37.7	12762	12840	78	.6
Wyoming.								
Uinta County	11565	5.7	5.3	37.7	12580	12451	—129	—1.0

Mean algebraic error in 20 samples..... —.3
Maximum negative error..... 1.6
Maximum positive error..... 1.0

Description. Bituminous coal. Illinois field—	Lab. No.	Proximate analysis air dried. Moisture. Per cent.	Ash. Per cent.	Volatile matter. Per cent.	Calorific value air dried. Determined. B. t. u.	Calculated. B. t. u.	Difference. B. t. u.	Error in calculated calorific value. Per cent.
Grundy County.								
Bed No. 2	14926	5.9	6.0	40.0	12290	12206	— 84	—.7
La Salle County.								
Bed No. 2	14923	5.1	9.7	41.9	12092	12139	47	.4
Bed No. 2	14922	6.8	9.5	41.0	11808	11732	— 76	—.6
Bureau County.								
Bed No. 2	14921	5.2	9.5	40.1	12078	11974	—104	—.9
Clinton County.								
Bed No. 6	14712	8.4	10.3	37.5	11313	11302	— 11	—.1
Bed No. 6	14711	7.8	10.7	38.5	11324	11365	39	.3
Randolph County.								
Bed No. 6	14710	5.8	12.1	38.9	11399	11376	— 23	—.2
St. Clair County.								
Bed No. 6	14709	5.3	11.6	41.1	11700	11531	—169	—1.4
Bed No. 6	14708	6.6	10.6	41.4	11637	11529	—108	—.9
Bed No. 6	14706	4.5	10.7	42.3	11923	11878	— 45	—.4
Montgomery County.								
Bed No. 6	14704	6.2	11.7	59.9	11534	11493	— 41	—.4
Sangamon County.								
Bed No. 6	14703	5.9	10.2	40.7	11691	11905	204	1.7
Bed No. 6	14702	8.4	10.8	39.6	11122	11137	15	.1
Bed No. 6	14701	7.9	9.1	40.7	11527	11515	— 12	—.1
Madison County.								
Bed No. 6	14700	9.0	10.5	40.2	11164	11084	— 80	—.7
Bed No. 6	14699	8.0	11.0	40.2	11322	11201	—121	—1.0
Williamson County.								
Bed No. 6	14697	5.3	8.7	37.3	12299	12164	—135	—1.1
Bed No. 6	14696	6.8	8.1	33.9	12159	12049	—110	—.9
Bed No. 6	14695	6.8	7.4	34.9	12258	12094	—164	—1.3
Bed No. 6	14694	7.2	9.5	33.0	11902	11893	— 9	.1
Franklin County.								
Bed No. 6	14692	5.3	10.8	35.4	11974	12163	109	1.5
Bed No. 6	14691	6.4	7.9	34.5	12253	12256	3	0
Bed No. 6	14690	4.6	13.2	40.0	11749	11936	187	1.6
Fulton County.								
Bed No. 5	14688	4.5	12.9	39.1	11633	11821	188	1.6
Bed No. 5	14687	5.7	12.0	33.7	11500	11657	157	1.4

Mean algebraic error in 30 samples..... —.1
Maximum negative error..... 1.4
Maximum positive error..... 1.7

Description. Bituminous coal. Appalachian field, Pennsylvania—	Lab. No.	Proximate analysis dry basis. Moisture. Per cent.	Ash. Per cent.	Volatile matter. Per cent.	Calorific value dry basis. Determined. B. t. u.	Calculated. B. t. u.	Difference. B. t. u.	Error in calculated calorific value. Per cent.
Allegheny County.								
Pittsburgh Bed	14879	3.3	6.4	36.2	13619	13799	180	1.3
Pittsburgh Bed	14855	2.7	5.6	37.2	13820	13629	9	.1
Pittsburgh Bed	14849	1.9	5.1	37.0	14008	14159	151	1.1
Pittsburgh Bed	13389	2.4	4.7	36.7	14058	13999	— 59	—.4
Pittsburgh Bed	12579	2.7	14.9	34.9	12325	12323	— 2	0
Pittsburgh Bed	12578	3.4	5.3	35.9	13734	13777	43	.3
Pittsburgh Bed	12577	3.2	8.5	34.6	13279	13322	43	.3
Pittsburgh Bed	12576	2.9	5.6	37.0	13817	13921	104	.8
Pittsburgh Bed	12574	3.0	5.4	37.7	13806	13925	119	.8
Pittsburgh Bed	12573	3.1	5.8	36.8	13738	13705	— 33	—.3
Pittsburgh Bed	12572	2.9	5.7	36.2	13761	13889	128	.9
Westmoreland County.								
Pittsburgh Bed	12853	2.5	10.4	30.3	13365	13450	85	.6
West Virginia—Marshall County.								
Pittsburgh Bed	14488	3.4	7.0	41.6	13313	13279	— 34	—.3
Kentucky.								
Bed No. 9	13260	3.1	7.6	37.8	12208	12191	— 7	—.1
Tennessee.								
Anderson County	13290	1.9	8.6	35.0	13777	13862	85	.6
Anderson County	13265	1.5	9.2	35.9	13615	13534	— 81	—.6
Anderson County	13264	1.7	10.1	35.0	13462	13559	97	.7
Anderson County	13238	1.9	11.5	33.0	13151	13250	99	.7
Anderson County	13237	1.6	6.6	35.4	14047	14011	— 36	—.3
Alabama.								
Shelby County	13466	3.9	7.5	35.1	13343	13370	27	.2
Shelby County	13465	5.8	7.5	34.1	13298	13408	110	.8
Shelby County	13464	2.6	4.9	35.4	14202	14067	—135	—.9
Shelby County	13463	2.1	4.0	36.5	14447	14225	—222	—1.5
Walker County	13462	3.8	9.4	37.7	12895	12841	— 51	—.4
Walker County	13461	3.0	9.1	39.7	13118	13279	161	1.2
Walker County	13460	4.6	13.2	35.9	12056	12201	148	1.2
Walker County	13459	3.7	9.3	37.9	12992	12946	— 46	—.4
Walker County	13187	1.1	16.1	26.4	12793	12825	32	.2
Walker County	13186	1.0	4.9	29.8	14647	14742	95	.7
Walker County	13185	2.0	5.0	35.5	13997	13968	— 19	—.1

Mean algebraic error in 30 samples..... .2
Maximum negative error in 30 samples..... 1.5
Maximum positive error in 30 samples..... 1.3

Description.	Lab. No.	Proximate analysis dry basis. Moisture. Per cent.	Ash. Per cent.	Volatile matter. Per cent.	Calorific value dry basis. Determined. B. t. u.	Calculated. B. t. u.	Difference. B. t. u.	Error in calculated calorific value. Per cent.
Semi-bituminous coal, Appalachian field, Pennsylvania—								
Cambria County.								
"B" Bed	14243	2.7	4.6	18.1	14560	14645	85	.6
"B" Bed	12377	.8	6.7	20.4	14549	14537	— 12	—.1
"B" Bed	12376	.8	9.4	21.4	14022	14207	185	1.3
"B" Bed	12375	.8	6.3	20.8	14531	14683	152	1.0
"B" Bed	12374	.8	6.1	20.0	14605	14688	83	.6
Indiana County.								
"E" Bed	12373	1.0	9.1	26.1	13945	14038	93	.7
Cambria County.								
"B" Bed	12372	.8	7.2	22.9	14443	14575	132	.9
"B" Bed	12371	.8	9.1	23.9	14040	14116	76	.5
"B" Bed	12370	.9	6.7	23.1	14485	14575	90	.6
"C" Bed	12369	.9	8.9	18.4	14081	14157	76	.5
Clearfield County.								
"B" Bed	12368	.8	10.9	20.4	13734	13876	42	.3
"B" Bed	12367	.9	9.0	21.6	14060	14198	138	1.0
West Virginia, McDowell County.								
Pocahontas Bed	14424	2.0	6.8	17.8	14324	14504	180	1.3
Pocahontas Bed	14420	1.6	5.9	18.0	14508	14598	90	.6
Pocahontas Bed	14399	2.8	4.6	17.7	14573	14663	90	.6
Pocahontas Bed	14282	4.2	3.2	18.6	14629	14551	— 78	—.5
Pocahontas Bed	14276	3.8	3.2	18.3	14690	14791	101	.7
Mercer County.								
Pocahontas	14260	3.1	3.9	18.2	14688	14823	135	.9
Pocahontas	14237	3.2	3.7	17.0	14729	14848	19	.1
McDowell County.								
Beckley Bed	14472	2.2	8.9	17.3	13952	14058	106	.8
Beckley Bed	14430	2.6	8.2	17.2	14006	14137	131	.9
Beckley Bed	14408	2.2	8.4	16.4	14006	14017	11	.1
Beckley Bed	14269	2.3	11.1	16.8	13514	13727	213	1.6
Raleigh County.								
Beckley Bed	14291	3.3	4.3	19.0	14519	14627	108	.7
Beckley Bed	14309	2.2	3.5	17.2	14738	14855	117	.8
Beckley Bed	14317	3.3	3.3	17.4	14704	14839	135	.9
Beckley Bed	14318	3.7	2.9	17.2	14668	14816	148	1.0
Fayette County.								
Sewell Bed	14404	3.0	3.1	25.7	14605	14717	112	.8
Sewell Bed	14362	3.0	3.8	28.0	14423	14512	89	.6
Sewell Bed	14345	2.9	2.3	25.6	14796	14854	58	.4

Mean algebraic error in 30 samples..... .7
Maximum negative error in 30 samples..... 1.6
Maximum positive error in 30 samples..... .5

Description.	Lab. No.	Proximate analysis dry basis. Moisture. Per cent.	Ash. Per cent.	Volatile matter. Per cent.	Calorific value dry basis. Determined. B. t. u.	Calculated. B. t. u.	Difference. B. t. u.	Error in calculated calorific value. Per cent.
Anthracite—								
Pennsylvania	14765	4.0	12.2	8.9	12591	12555	— 36	—.3
Pennsylvania	14761	3.9	14.7	8.5	12179	12231	52	.4
Pennsylvania	14763	4.9	15.4	9.5	11951	12047	93	.6
Pennsylvania	14762	3.2	16.4	8.0	11939	12020	81	.7
Pennsylvania	14761	3.2	11.5	9.3	12971	13043	72	.6
Pennsylvania	14760	1.6	19.7	12.2	11929	12001	72	.6
Pennsylvania	14759	.9	18.8	12.1	12227	12416	189	1.5
Pennsylvania	11758	3.8	18.4	7.1	12333	11392	59	.5
Pennsylvania	14757	1.7	17.6	10.7	12136	12238	102	.8
Pennsylvania	14720	2.0	17.9	8.1	11875	11920	47	.4
Pennsylvania	14719	2.7	19.7	8.4	11578	11662	84	.7
Pennsylvania	14718	3.1	16.2	8.9	11916	11990	74	.6
Pennsylvania	14520	3.0	15.1	6.4	12038	12125	87	.7
Pennsylvania	14209	3.8	17.1	8.2	11781	11777	— 4	0
Pennsylvania	14208	3.6	14.4	7.2	12137	12222	85	.7
Pennsylvania.								
Sullivan County	9664	3.6	11.9	9.1	13072	13212	140	1.1
Sullivan County	9665	3.4	11.5	8.5	13156	13273	117	.9
Sullivan County	9652	3.4	11.7	9.3	13120	13221	101	.8
Sullivan County	9653	3.7	13.1	9.2	12836	12870	34	.3
Sullivan County	9654	3.4	15.6	8.4	12497	12569	72	.6

Mean algebraic error in 20 samples..... .6
Maximum negative error in 20 samples..... .3
Maximum positive error in 20 samples..... 1.5

A total of 176 analyses were selected at random from the records of the chemical laboratory without any attempt whatever towards selecting concordant or diverging results, but simply taking them from the laboratory record as they happened to occur. Enough analyses were selected to secure about 20 to 30 samples of each representative class of coal from the most recent lignites, through the range of sub-bituminous, bituminous, semi-bituminous and anthracite coals of Pennsylvania. For comparison a number of peats are also included.

The tabulation brings out in a striking manner the variation in the relation between the heating value calculated by Dulong's formula and the true heating value as determined in the bomb calorimeter. This relation is within certain limits, characteristic of the class of coal. For instance, in coals low in volatile matter and oxygen, like anthracite and Pocahontas coal, the calculated value is usually from .3 to 1.5 per cent greater than the determined value. In only very few instances is the calculated value less than the determined value; in the bituminous coals the calculated values vary both above and below the determined values usually within limits of 1.5 per cent; in sub-bituminous and lignitic coals the calculated value becomes less and less and less than the determined value as the oxygen increases; the deviation of ten reaching 4 and 5 per cent; in peat the calculated results are quite unreliable, the results being from 3 to 11 per cent low.

A summary of Table II, giving the maximum, minimum and mean error in the calculated values, together with the average moisture and ash free oxygen for each class of coal, is given in Table III.

on the constancy in heating value of the "combustible" or coal substance free of moisture and ash.

The calorific value of coal may be referred to a moisture-and-ash free basis by dividing the calorific value as determined by one minus the sum of the moisture and ash in the unit weight of fuel.

$$\text{Moisture and ash free calorific value} = \frac{\text{Calorific value as determined}}{1 - \frac{\text{per cent moisture plus per cent ash}}{100}}$$

This so-called moisture-and-ash free calorific value, which represents approximately the heating power of the combustible in the coal, has been found fairly constant for the same coal bed over limited areas, such as are covered by several adjacent mines.

In Table IV are given some "moisture-and-ash free" calorific values of mine samples taken by engineers of the bureau at different points in a number of mines in Pennsylvania. They are typical in showing the usual range of variation that is found in samples from different parts of a mine.

TABLE III.—SUMMARY OF THE MEAN ALGEBRAIC MAXIMUM POSITIVE AND MAXIMUM NEGATIVE ERRORS, IN THE CALORIFIC VALUES CALCULATED BY DULONG'S FORMULA, AS FOUND IN GROUPS OF 20 TO 30 REPRESENTATIVE ANALYSES OF EACH CLASS OF COAL.

	Error in calculated calorific value.			Oxygen in coal.
Class of coal—	Mean algebraic error. Per cent.	Maximum plus error. Per cent.	Maximum minus error. Per cent.	Moisture and ash free. Per cent.
Peat	—7.4		11.0	34.4
Lignite—Dakotas, Montana and Texas	—3.1		5.4	23.4
Sub-bituminous—Rocky Mountain field	—1.4	.9	3.8	19.1
Bituminous—Rocky Mountain field	—.3	1.0	1.6	9.8
Bituminous—Illinois field	—.1	1.7	1.4	10.7
Bituminous—Appalachian field	.2	1.3	1.5	7.1
Semi-bituminous—Pennsylvania and West Virginia	.7	1.6	.5	3.1
Anthracite—Pennsylvania	.6	1.5	.3	3.1

The progressive change in the Dulong values, with the increase in oxygen, is significant and points to a combination of part of the oxygen with carbon in highly oxygenated coals. Porter and Ovitz[6] have already arrived at this conclusion from a consideration of data obtained in their studies of the volatile matter obtained by destructive distillation.

CALCULATION OF CALORIFIC VALUE FROM THE PROXIMATE ANALYSES.

The calculation of calorific values by formulae depending on the proximate analysis is apt to give quite erroneous results. Such methods are subject to the considerable uncertainty of the fixed carbon and volatile matter determinations. Furthermore, the variable proportion of inert volatile matter, which does not contribute to the heating value, is not taken into consideration.

Use of "Moisture-and-Ash-Free" Values.—A fairly accurate and simple method of calculating the heating value of Appalachian, bituminous, and semi-bituminous coal from the same mine and seam, is based

In the latter part of Table IV are given some data on the variation in "moisture-and-ash free" calorific values that have been found in car samples of coal delivered to the power plant of the Pittsburgh Experiment Station for fuel purposes. While each set of cars grouped together is supposed to have come from the same mine, they were not loaded under the inspection of representatives of the bureau; also, the coal may have had more or less opportunity for weathering the transit to the testing station. This would explain the slightly larger variations in the car samples.

The greatest deviation in "moisture-and-ash free" calorific value of any one individual sample from the average of the mine is usually less than one per cent. In only two cases does it reach the maximum figure of 1.1 per cent. Obviously the calorific value of samples representing various shipments of coal from the same mine and seam can be calculated with an accuracy of about 1 per cent by multiplying the average "moisture-and-ash free" calorific value of the coal by 1 minus the sum of the moisture and ash of the various individual samples. This method of calculating

[6]Porter, H. C., and Ovitz, F. K., The Volatile Matter of Coal; Bull. No. 1, Bureau of Mines, 1910.

TABLE IV—VARIATION IN "MOISTURE-AND-ASH FREE" CALORIFIC VALUES OF MINE SAMPLES FROM THE SAME MINE.

Locality and coal bed.	"Moisture-and-ash free" calorific values of individual samples. B. t. u.	Average. B. t. u.	Maximum difference of individual samples. B. t. u.	Maximum difference of individual samples. Per cent.	Maximum deviation from average. B. t. u.	Maximum deviation from average. Per cent.
5 samples from a mine near Pigort, Pa., in Cambria Co., Middle Kittanning Bed	15600 15600 15640 15610 15650	15620	50	.3	30	.2
5 samples from a mine near Barnesboro, Pa., in Cambria Co., Lower Kittanning or "B" Bed	15710 15670 15830 15760 15660	15726	170	1.1	104	.7
5 samples from a mine near Carrolton, Pa., in Cambria Co., Lower Kittanning or "B" Bed	15670 15660 15740 15670 15820	15712	160	1.1	108	.7
27 samples from mines near Twin Rocks, Pa., in Cambria Co., Lower Kittanning or "B" Bed	15820 15730 15890 15780 15730 15710 15770 15820 15700 15800 15690 15700 15740 15770 15840 15720 15760 15740 15740 15760 15790 15770 15840 15750 15780 15830 15820	15770	200	1.3	120	.8
10 samples from two adjacent mines near Clymer, Pa., in Indiana Co., Lower Kittanning or "B" Bed	15680 15700 15750 15610 15710 15740 15740 15650 15710 15700	15700	140	.9	90	.6
5 samples from a mine near Beaverdale, Pa., Cambria Co., Lower Kittanning or "B" Bed	15741 15768 15721 15772	15752	51	.3	31	.2
5 samples from a mine near El Moro, Pa., in Cambria Co., Lower Kittanning or "B" Bed	15763 15862 15611 15772 15887	15779	276	1.8	169	1.1
4 samples from a mine near Masontown, Preston Co., W. Va., Upper Freeport Bed	15490 15470 15380 15460	15450	110	.8	70	.5
5 samples from a mine near Richard, Monongalia Co., W. Va., Upper Freeport Bed	15530 15500 15470 15400 15510	15482	130	.9	82	.1
6 samples from a mine near Barnesboro, Pa., Cambria Co., Lower Freeport Bed	15600 15570 15600 15660 15640 15650	15620	90	.6	40	.3
9 samples from a mine near Spangler, Pa., Cambria Co., Lower Freeport Bed	15671 15651 15644 15656 15727 15678 15623 15705 15700	15662	204	1.3	139	.9
10 samples from a mine near Hastings, Pa., Cambria Co., Lower Freeport Bed	15698 15678 15646 15588 15604 15590 15655 15638 15608 15647	15635	110	.8	63	.1
4 samples from a mine near Dante, Russell Co., Va., Upper Banner Bed	15426 15521 15408 15476	15458	113	.8	63	.1
23 samples from the government experimental mine near Bruceton, Pa., Allegheny Co., Pittsburgh Bed	15440 15490 15470 15410 15460 14960	15087	260	1.7	157	1.0

Locality and coal bed.	"Moisture-and-ash free" calorific values of individual samples. B. t. u.	Average. B. t. u.	Maximum difference of individual samples. B. t. u.	Maximum difference of individual samples. Per cent.	Maximum deviation from average. B. t. u.	Maximum deviation from average. Per cent.
Car samples from 27 cars of coal delivered to testing station from Dec., 1910, to May, 1911, from a mine near Meadowlands, Washington Co., Pa., Pittsburgh Bed	14930 15030 15070 15080 15040 15040 15070 15140 15070 15080 15140 15140 15140 15100 15060 15050 15080 14800 14910 14890 15040 14760 14950 14880 14880 14840 14900 14870 14860 14800 14830 14920 14800 14900 14810 14990 14840 14880 14880 14910 14850 14950 14840 14900	14874	280	2.0	166	1.1
Car samples from 4 cars of coal delivered to testing station from Dec. 19, 1910, to Jan., 1911, from another mine near Meadowlands, Washington Co., Pa., Pittsburgh Bed.	14560 14640 14640 14630	14618	80	.6	58	.4
Car samples from 7 cars of coal delivered to testing station from May, 1911, to July, 1911, from a mine near Burgettstown, Washington Co., Pa., Pittsburgh Bed	14750 14680 14690 14790 14650 14750 14890	14743	240	1.6	147	1.0
Car samples from 44 cars of coal delivered to testing station from Aug., 1911, to April, 1912, from a mine near Arnold, Westmoreland Co., Pa., Upper Freeport Bed	15180 15250 15180 15200 15190 15260 15240 15280 15190 14250 15300 15220 15170 15210 15290 15210 15220 15220 15180 15240 15100 15180 15220 15250 15190 15180 15220 15190 15220 15210 15300 15250 15290 15250 15280 15300 15100 15270 15230 15250 15230 15280 15250 15220	15226	200	1.3	126	.8
Car samples from 5 cars of coal delivered to testing station from Nov., 1911, to June, 1912, from a mine near Monongahela City, Westmoreland Co., Pa., Pittsburgh Bed	15280 15140 15150 15210 15150	15186	140	.9	94	.6
Car samples from 3 cars of coal delivered to testing station from Nov., 1911, to May, 1912, from a mine near Greensburg, Westmoreland Co., Pa., Pittsburgh Bed	15350 15310 15400	15353	90	.6	47	.3

will not apply to weathered coals, which on account of absorption of oxygen, have lost some of their original heating value, or to coals that vary considerably in the character and amount of ash and sulphur. In the coals cited in table 4 the ash is usually less than 12 per cent and the sulphur less than 2.0 per cent.

Where the sulphur content is larger and more variable, as found in some of the coals of Ohio[7] and Illinois[8], a further correction for the influence of sulphur should be applied.

[7]Lord, N. W., Coal, Bull. 9, 4th Lines, Geological Survey of Ohio (1908), pp. 268.

[8]Parr, S. W., Bull. 16 Illinois State Geological Survey (1909), pp. 212.

SAMPLING.

The chemist makes his analysis on a few ounces of powdered coal. If the analysis is to be of any value, this small sample must have a composition that is an average of the entire lot of coal whose value is to be established. Non-representative samples are misleading and frequently lead to much controversy as well as financial loss. Therefore, sampling should never be placed in inexperienced hands. It is just as important for the chemist to devise and direct the method of taking samples as it is for him to make the analysis. The sampling of shipments and deliveries of coal involves special difficulties on account of the usual admixture of pieces of slate, bone and other impurities with the lumps of coal. The mechanical methods which have been found satisfactory in sampling ore cannot be used for the ordinary sizes of coal on account of destroying the value of the fuels by the necessary crushing. The accuracy of sampling the commercial sizes of coal is limited to the amount and size of the largest lumps of impurities and the quantity of original sample that can be taken without incurring too great a cost. The accuracy of any method of sampling should be frequently tested by taking two or more independent samples, which are reduced and analyzed separately. Ordinarily the sample sent to the laboratory will weigh from three to five pounds, and will be pulverized to about ¼-in. size. The original gross sample, which may amount to 500 or 1,000 pounds, must be pulverized, mixed and quartered in such a manner as to maintain the same relative proportions of coal and impurities until the final 3 to 5-pound sample is obtained; furthermore, coal has a marked tendency to lose moisture in crushing; this must be avoided as much as possible.

The final sample should be placed in a moisture-proof container for shipment to the laboratory. Wooden boxes or sacks should never be used for samples in which moisture is to be determined.

ACCURACY OF MINE SAMPLING.

During the past nine years the U. S. Geological Survey and its successor, the Bureau of Mines, has analyzed a large number of mine samples of coal, taken in connection with the investigation of coal as it occurs in the mine. These samples[9] are taken by cutting down a section or groove of uniform cross-section across the face of the seam. The gross sample, amounting to about 6 lbs. for each foot in thickness of the coal bed, is pulverized to pass a ½-in. screen, mixed and quartered down to about 3 lbs., which is placed in a galvanized iron can, sealed moisture tight, and mailed to the laboratory.

In taking these samples some uniform system of including and rejecting the partings or bands of impurities that occur in coal beds is essential. Usually partings more than ⅜ in. thick and lenses or concretions of "sulphur" or other impurities more than two inches in maximum diameter and ½ in. thick are excluded. By following such a system the analytical results are comparable in representing the quality of coal in different coal beds, it is quite necessary to complete the sampling and seal the sample can at the face as quickly as possible after breaking down the coal in order to avoid loss of moisture.

These mine samples usually represent a better quality of coal than is ordinarily shipped from the mine, as in the operation of a mine it is not practicable to use the same care in excluding partings and other impurities. They are of value in showing the quality of coal as it occurs in the seam, at the point of sampling; and the results are subject to the unavoidable variations due to including more or less of the partings and the errors in reducing the gross sample to three pounds. It is possible to practically eliminate the errors of reducing the gross sample by crushing the entire quantity of coal cut down from the face to less than 4-mesh size, and then mixing and quartering to 3 pounds. However, such a procedure is of doubtful value on account of the greater errors resulting from the inclusion of more or less of the partings in cutting down the section, especially where they tend to crumble from the action of the pick.

There is also to be considered the variation in the proportion of impurities in neighboring sections; the extent of this variation is usually greater than the errors incurred in sampling the individual section.

In Table V are shown the results of a series of duplicate 3-lb. can samples that were taken by the standard method of the Bureau of Mines, as described in Technical Paper 1.[10]

The entire sample which had been cut from the face was crushed to pass a ½-in. screen, mixed and quartered to 3 lbs., which was called Sample No. 1; the rejected portions were then combined, mixed and again quartered to 3 lbs., which was called Sample No. 2. Both samples were sent to the laboratory in the usual galvanized iron sample cans, which are closed with a screw cap and made moisture tight by wrapping the joint with electrician's tape. The samples were air dried, pulverized in the usual manner by rolls and ball mill and separately analyzed. The results obtained for total moisture, ash and sulphur are given in the table.

On account of the high percentage of moisture, ash and sulphur, and the irregular distribution of the impurities in the seam, Illinois coals are unusually difficult to sample. Yet in spite of the high moisture content, the greatest difference of moisture in duplicate samples was only 3 per cent, with an average for the 30 sections of 0.1 per cent.

In the four sections in the experimental mine the maximum difference was .1 per cent and the average difference was .05 per cent.

[9]Method of taking mine samples is described in detail in Bureau of Mines Technical Paper 1: Sampling Coal in the Mine, by J. A. Holmes.

[10]Holmes, J. A. Sampling Coal in the Mine. Technical Paper 1, Bureau of Mines.

TABLE V—A COMPARISON OF DUPLICATE 3-LB. SAMPLES TAKEN FROM THE SAME SECTION OF COAL.

Location of mine.	Total moisture. Sample 1 per cent.	Total moisture. Sample 2 per cent.	Total moisture. Difference per cent.	Ash. Sample 1 per cent.	Ash. Sample 2 per cent.	Ash. Difference per cent.	Sulphur. Sample 1 per cent.	Sulphur. Sample 2 per cent.	Sulphur. Difference per cent.
Danville, Vermillion Co., Ill.—									
Section A	12.4	12.4	0.0	7.8	7.9	0.1	2.9	3.0	0.1
Section B	13.1	13.2	0.1	10.0	9.9	0.1	4.0	3.5	0.5
Composite	12.8	12.7	0.1	8.8	8.8	0.0	3.5	3.2	0.3
Westville, Vermillion Co., Ill.—									
Section A	13.3	13.2	0.1	8.5	9.2	0.7	2.3	2.4	0.1
Section B	15.3	15.5	0.2	7.9	8.0	0.1	1.6	1.7	0.1
Section C	16.2	16.2	0.0	8.2	8.3	0.1	1.8	1.8	0.0
Section D	14.8	14.9	0.1	8.7	8.5	0.2	1.9	2.0	0.1
Section E	15.5	15.4	0.1	7.1	8.7	1.6	1.5	2.8	1.3
Section F	15.2	15.1	0.1	8.6	8.7	0.1	2.9	2.9	0.0
Composite	15.1	15.1	0.0	8.2	8.5	0.3	2.1	2.3	0.1
Georgetown, Vermillion Co., Ill.—									
Section A	15.2	15.1	0.1	9.8	9.7	0.1	2.0	2.1	0.1
Section B	15.4	15.5	0.1	11.2	10.9	0.3	1.9	1.9	0.0
Section C	15.9	15.7	0.2	11.6	12.2	0.6	2.4	2.6	0.2
Composite	15.5	15.5	0.0	10.9	11.0	0.1	2.1	2.2	0.1
Danville, Vermillion Co., Ill.—									
Section A	13.1	13.0	0.1	10.0	9.8	0.2	3.2	3.1	0.1
Section B	12.9	12.8	0.1	9.3	9.3	0.0	3.7	3.5	0.2
Section C	12.7	12.7	0.0	9.7	9.6	0.1	3.7	3.4	0.3
Section D	12.6	12.5	0.1	9.1	8.8	0.3	3.1	2.9	0.2
Section E	13.9	13.8	0.1	9.1	9.7	0.6	3.1	2.8	0.3
Section F	13.8	13.8	0.0	8.5	8.5	0.0	2.9	3.0	0.1
Composite	13.0	13.1	0.1	9.3	9.2	0.1	3.2	3.2	0.0
Fairmont, Vermillion Co.—									
Section A	14.2	14.1	0.1	9.6	9.9	0.3	2.2	2.3	0.1
Section B	13.6	13.5	0.1	9.1	9.8	0.7	2.1	2.3	0.2
Section C	13.4	13.1	0.3	11.3	11.4	0.1	2.6	2.8	0.2
Composite	13.7	13.6	0.1	10.0	10.4	0.4	2.3	2.4	0.1
Steelton, Vermillion Co., Ill.—									
Section A	15.9	15.8	0.1	10.7	10.3	0.4	2.4	2.6	0.2
Section B	14.2	14.2	0.0	9.9	10.0	0.1	2.2	2.5	0.3
Section C	14.9	14.6	0.3	8.5	8.7	0.2	2.3	2.5	0.2
Composite	15.0	14.8	0.2	9.8	9.7	0.1	2.3	2.5	0.2
DuQuoin, Perry Co., Ill.—									
Section A	10.4	10.7	0.3	9.6	9.0	0.4	0.8	0.8	0.0
Section B	11.5	11.6	0.1	8.7	9.0	0.3	0.8	0.9	0.1
Section C	10.7	10.9	0.2	10.6	10.8	0.2	0.9	1.0	0.1
Section D	10.5	10.6	0.1	12.2	11.7	0.5	1.0	0.9	0.1
Section E	10.1	10.3	0.2	11.6	11.8	0.2	0.9	0.8	0.1
Section F	10.8	10.7	0.1	11.0	11.5	0.5	0.8	0.8	0.0
Composite	10.7	10.7	0.0	10.7	10.6	0.1	0.9	0.9	0.0
Bruceton, Allegheny Co., Pa., Pittsburgh Bed—									
Section A	2.9	2.8	0.1	5.7	5.6	0.1	1.1	1.1	0.0
Section B	3.0	3.0	0.0	6.0	5.8	0.2	1.2	1.2	0.0
Section C	2.8	2.7	0.1	5.1	5.2	0.1	1.0	1.1	0.1
Section D	2.7	2.7	0.0	5.5	5.7	0.2	1.2	1.2	0.0
Composite	2.8	2.8	0.0	5.6	5.6	0.0	1.1	1.1	0.0
Colver, Cambria Co., Pa., Miller or "B" Bed—									
Section A	....	....	...	5.4	5.2	0.2	1.0	1.0	0.0
Section B	....	....	...	4.9	4.7	0.2	0.9	0.9	0.0
Section C	....	....	...	5.1	5.2	0.1	1.0	1.1	0.1
				5.1	5.0	0.1	1.0	1.0	0.0

	Moisture Per cent.	Ash Per cent.
Maximum difference in duplicate mine samples taken in Illinois	0.3	1.6[1]
Maximum difference in samples taken in Pennsylvania	0.1	0.2
Average difference in samples taken in Illinois	0.1	0.3
Average difference in samples taken in Pennsylvania	0.05	0.16

[1]Next highest difference in Illinois samples was 0.7.

The average variation in ash of the duplicate samples from seven sections in two Pennsylvania mines is .1 per cent; the maximum variation being .2 per cent.

In the Illinois series the average ash variation is 0.3 per cent and the maximum variation is 1.6 per cent; the next highest difference is 0.7 per cent.

In an investigation of the quality of coal in the mine several samples should be taken at different places. These may be separately analyzed or combined at the laboratory into a composite sample. The composite analysis of several samples is subject to smaller sampling errors than the individual samples. For example, in Table V the largest ash variation in the composite analyses of samples 1 and 2 is 0.4 per cent. although several individual pairs of duplicate samples

showed 0.7 per cent difference, and one pair out of the 36 had a difference of 1.6 per cent.

SAMPLING IN THE LABORATORY.

Next in importance to securing a representative sample to send to the laboratory is the further treatment in the laboratory sampling room by which a representative powdered sample is obtained for analysis.

In the method used by the Bureau of Mines, moisture loss is avoided by air drying the 3-lb. sample before pulverizing. The amount of moisture expelled during the air drying process is recorded and added to the final moisture obtained by drying the powdered sample at 105° C. (221° F.). The air dry sample is quickly pulverized to 10 mesh by passing through a roll crusher, reduced on a riffle sampler to about 450 grams (1 lb.) and ground to 60 mesh in a moisture-tight ball mill, which consists of rotating porcelain jars containing well-rounded flint pebbles. The final powdered sample is preserved in a rubber stoppered bottle to prevent change in moisture content.

This method of sampling was developed by Lord and Somermeier at the U. S. Fuel Testing Plant at St. Louis. Numerous experiments have shown that this method reduces the unaccounted for moisture changes during sampling and analysis to a lower point than any other practicable method that has yet been devised. The very uniform moisture results obtained on the duplicate mine samples of the high moisture Illinois coals cited in Table V could not have been obtained by the old methods of pulverizing on a bucking board, where the exposure of finely divided coal to a dry or humid atmosphere could change its moisture content.

Usually the laboratory sampling error with respect to ash, by the method just described, is less than .3 per cent, and seldom greater than .5 per cent. Where careful work is done by the sampler the .5 per cent limit should not be exceeded. In table 6 are given some results of duplicate sampling, as illustrating the usual errors.

TABLE VI—A COMPARISON OF MOISTURE AND ASH IN DUPLICATE 3-OZ. POWDERED SAMPLES MADE FROM THE 3-LB. SAMPLES RECEIVED AT THE LABORATORY.

	Per cent moisture in air dry coal.			Per cent Ash in air dry coal.		
Laboratory No.	Sample A.	Sample B.	Difference.	Sample A.	Sample B.	Difference.
14807.....	1.95	2.02	.07	12.93	12.78	.15
14808.....	2.11	2.09	.02	12.52	12.53	.01
14809.....	6.90	6.81	.09	13.40	13.12	.28
14812.....	1.89	1.91	.02	12.55	12.70	.15
14813.....	.92	.92	.00	6.10	6.36	.26
14814.....	.66	.69	.03	8.45	8.32	.13
14815.....	3.57	3.67	.10	16.64	16.27	.37
14817.....	1.14	1.22	.08	15.36	15.49	.13
14818.....	1.63	1.65	.02	10.63	10.47	.16
14819.....	1.08	1.19	.11	9.00	8.83	.17
Average difference.....			.05			.18
Max'um diff. in 10 samples			.11			.37

PREPARATION OF LABORATORY SAMPLES WITHOUT PRELIMINARY AIR DRYING.

Where the highest degree of accuracy with respect to moisture is not required, and where the analyses must be had in the shortest possible time, the method used in the inspection laboratory of the Bureau of Mines will give satisfactory results.[11] This method consists in rapidly crushing the coarse sample to 20 mesh by means of a roll crusher or coffee mill type of grinder and taking a representative portion of this product for the determination of total moisture. The remainder and main portion of the sample is then mixed and divided with a riffle sampler to not less than 150 grams, which is then pulverized to 60 mesh with any suitable apparatus, such as a bucking board or disc pulverizer, without regard to moisture losses. Both samples are preserved in rubber stoppered bottles.

The moisture determined in the 20-mesh sample represents the total moisture in the coal as received; the moisture in the final powdered sample is also determined in order to recalculate the analysis to the as received condition.

The results for moisture obtained by this method are somewhat low, due to unavoidable loss while crushing the coal to 20-mesh size. Wet coals must be partially air dried and the loss of weight noted.

INCORRECT METHODS OF PREPARING COAL SAMPLES.

The determination of total moisture by drying a portion of the coarse sample in a steam oven at about 105° C. (221° F.) will give low results, the error increasing with the size of the lumps.

The method of drying the coarse sample at temperatures above 100° C. (212° F.) and then pulverizing to a powdered sample for analysis, with the assumption that the powdered coal is dry coal, will give quite erroneous results. The powdered sample will never be dry, but will contain from .3 to 1.0 per cent moisture, which it has either failed to give up while drying in the coarse condition, or has taken up from the atmosphere, while being pulverized. The heating values are directly affected by the errors in the sampling and in the moisture determinations.

ABRASION IN BALL MILLS.

In using any apparatus for pulverizing samples the amount of contamination from abrasion of the pulverizing surfaces should always be investigated. Before the U. S. Fuel Testing Plant at St. Louis adopted the ball mill for the final grinding of coal samples, tests were made to determine whether there was danger of materially increasing the ash content of the samples from shipping and abrasion of the flint pebbles used in grinding. In these tests the weight of the sample ground each time on the ball mill was approximately 500 grams, and the abrasion of the pebbles (calculated as percentage of the weight of the samples

[11] The fuel inspection laboratory of the Bureau of Mines, by J. D. Davis, Bureau of Mines, Bull. No. 41 (1912), pp. 74.

ground) was determined from the loss in weight sustained by the pebbles. The results on these weighed lots of pebbles were as follows:

TABLE VII—LOSS* IN WEIGHT OF THREE LOTS OF FLINT PEBBLES USED FOR PULVERIZING COAL IN THE BALL MILL.

Lot.	Total wt. of samples ground, grams.	Weight of Pebbles. Before grinding, grams.	After grinding, grams.	Loss by Abrasion. Actual, grams.	Ratio to coal ground, per cent.
No. 1 (250 samples ground)	125,000	4118.6	4113.1	5.5	0.004
No. 2 (230 samples ground)	115,000	3502.9	3499.4	3.5	.003
No. 3 (245 samples ground)	122,500	4273.2	4268.3	4.9	.004

The results show only .004 per cent increase in ash due to the abrasion from the pebbles.

In order to determine the extent of abrasion from the porcelain jar, the following tests were made:

TABLE VIII—LOSS IN WEIGHT OF PORCELAIN JARS USED FOR PULVERIZING COAL IN THE BALL MILL.

	Total weight of samples ground, grams.	Weight of Jar. Before grinding, grams.	After grinding, grams.	Loss by Abrasion. Actual, grams.	Ratio to coal ground, per cent.
Jar No. 35 (100 samples of 150 grams each ground)	15,000	8,095	8,085	10.0	.066
Jar No. 37 (100 samples of 150 grams each ground)	15,000	8,317	8,314	3.0	.020
Jar No. 35 (100 samples of 300 grams each ground)	30,000	8,085	8,075	10.0	.033
Jar No. 37 (100 samples of 300 grams each ground)	30,000	8,314	8,310	4.0	.013
Jar No. 36 (30 samples of 300 grams each ground)	9,000	10,789	10,788	1.0	0.11

Evidently there is a little more abrasion from the porcelain jars than from the pebbles. In the experiments the same amount of material was abraded in 150-gram samples as in 300-gram samples, hence the necessity of using large samples. Five hundred grams is the best amount, and should not cause the ash content to be raised more than 0.04 per cent at the highest, which is less than the analytical error in the determination of ash.

TABLE IX—ASH IN COKE PULVERIZED BY THREE DIF- FERENT METHODS.

Laboratory No.	Ash in sample pulverized with bucking board, Per cent.	Ash in sample pulverized with diamond mortar, Per cent.	Ash in sample pulverized in ball mill, Per cent.	Difference in ash found in bucking board and ball mill, Per cent.	Difference in ash found in diamond mortar and ball mill., Per cent.
11033	12.9	11.8	11.5	1.4	.3
11034	12.9	11.4	10.8	2.1	.6
11035	12.8	10.3	10.5	2.3	—.2
11036	15.2	11.3	10.8	4.4	.5
11037	....	10.0	9.7	...	.3
11038	....	10.7	10.7	...	.0
11039	....	11.8	10.6	...	.2
11040	15.4	12.3	10.9	4.5	1.4
11041	....	10.3	10.1	...	.2
11042	....	10.2	9.7	...	.5
Average				2.9	.4

A more direct test of added ash from abrasion was made by placing 400 grams of ordinary granulated sugar in the mill and rotating it continuously for four hours. Before grinding the sugar contained .04 per cent ash; after grinding it contained .06 per cent ash, an increase of .02 per cent.

That the ball mill is the most satisfactory appliance for pulverizing coke is shown by the following experiments: Ten samples of a hard foundry coke weighing about 25 lbs. each were crushed to 10-mesh size by first passing through a chipmunk jaw crusher and then through a pair of steel rolls. Each sample was tions of about 8 lbs. each. The first portion was again put through the rolls until all of the 8 lbs. passed through a 20-mesh sieve, and was then mixed and reduced with the riffle to 150 grams, which was rubbed down to 60 mesh on a chilled cast iron bucking board. The second 8-lb. portion of each sample was also put through the rolls again until all passed the 20-mesh sieve; was then riffled down to 150 grams and pulverized to 60 mesh in a tool steel diamond mortar. The third 8-lb. portion of each sample was mixed and divided on the riffle to about 300 grams, which was then mixed and divided with a riffle into three portions then placed in the ball mill and pulverized to 60 mesh. Owing to the extreme hardness of this coke, 4 hours' rotation in the ball mill was required to pulverize to 60 mesh. After removing from the ball mill the entire sample was put through the 60-mesh sieve, mixed and reduced on the riffle to about 60 grams for analysis.

All the 60-mesh samples were tested for iron with a magnet. No magnetic particles were found in the ball mill sample, and only a few in the diamond mortar sample; the bucking board sample showed the

*Page 8, Bulletin No. 223, U. S. G. S. Experimental Work of Chemical Laboratory, U. S. Fuel Testing Plant, St. Louis, Mo., by N. W. Lord.

presence of considerable metallic iron. Ash determinations were made on each of the diamond-mortar and ball-mill samples and on some of the bucking board samples. The results are shown in Table IX.

With only one exception, the samples pulverized in the ball mill contained the least ash; the diamond mortar, which crushes by impact only, ranks second. Rubbing surfaces of chilled iron and even chrome steel, such as used in the bucking board and disc pulverizer, are abraded by the hard particles of coke, and therefore should never be used for the fine grinding of coke.

CONCLUSIONS.

To state definite limits of accuracy for coal analysis is almost impossible. The factors which influence the results are many and variable. They depend on the kind and quality of coal, the method of sampling and analysis, and the skill and experience of the analyst in the special field of coal testing.

With the exception of the volatile matter, fixed carbon and oxygen determinations, the best analytical methods are more accurate than the methods of sampling. The method of taking the original sample is often limited by commercial conditions. The determination of the heating value with the use of properly standardized calorimeters and thermometers is reliable and comparable. Appreciable errors, when such occur, are due to sampling or a change in the composition of the sample by oxidation or less of moisture. Finally, a statement of how the sample was taken should always go with the report of analysis. This will enable one who has a knowledge of coal to properly interpret the report of analysis.

TANNING PRODUCT.

The following extracts from the Calcutta Capital describe an Indian tanning material:

Sun-le-the is the Burmese name for the Caesalpinia digyna, Rotti, the pods of which, containing, as they do, from 50 to 60 per cent of tannin, are among the most valuabe tanning materials which are at present known to the world. Second to none but quebracho extract, with a tannin content of 70 per cent and that of "than," with more than 68, they are equal to gambier, "block" and "cube," and superior to sumach, the chebulic myrobalans, divi-divi, cutch and algarobilla. With the exception, then of the extract of "than," the product of the bark of the terminalia oliveri, brandis —the pods of sun-le-the alone can claim to be regarded as the most profitable source of commercial tannin in our indigneous flora. The presence, even in very large quantities of tannin in the tissues of a particular plant will not of itself help such a plant to be recognized as an important source of that product. The absence, at the same time, of deleterious coloring matters, the absence of undue fermentation in the steeping vats, the absence of "speckling" on the skins that are treated, the absence of glutinous or adhesive substances, these are some of the negative qualities which lend the positive value for which the finest tanning materials are prized. In all these qualities, the pods of sun-le-the, which are said "to yield leather as white as snow" and to be "chemically perfect as a tanning material," excel the other Indian "tans." The leather or skin tanned with their aid is equal in softness to that produced with the agency of the better known divi-divi pods, but superior in color, appearance and texture. Sun-le-the pods are, therefore, capable of being employed more extensively for tanning and are particularly valuable when the object is the production of light or bright colored high class leather. The principle underlying their action in the steeping vat is the union of the tannin, which appears to be laid in a remarkably pure and available condition, with the gelatin of the leather exposed to its influence and the consequent formation of a precipitate which in color has been likened to the whiteness of driven snow. The amount of tannin the pods contain is so great that they are astringent enough to yield a deep blue-black with ferric salts, a circumstance which clearly indicates their adaptability for the manufacture of writing ink.

These interesting pods, neglected now, are the product of a common wayside plant, a low growing, thorny scandent shrub which is wild in the hedgerows, waste lands and clearings near villages throughout the localities of its growth. Though it avoids situations that are flooded in the rains and usually thrives on fairly high land, it grows on the banks of rivers and forest streams and roadsides that skirt the feet of low hills. Though said to be found on the astern Himalaya, it is elsewhere essentially a low country plant. Its leaves, which are from six to nine inches in length, are freely divided like tamarind leaves; its racemes of flowers, in the axils of the leaves, appear in the middle of the southwest monsoons; and its pods, that are about two inches long, ripen in the months of April and May. For the highest purposes of their utilization, the pods should be gathered before they are ripe. When compared with their length, the pods are broad; but this dimension, though somewhat variable, seldom exceeds three-fourths of an inch. They are almost as thick as they are broad, with constrictions of the valves between the few seeds. The sutures, too, are remarkably thick and sinute at the constrictions between the seeds. The seeds themselves, about half an inch long, are nearly spherical in shape and dark greenish-brown in color. There are seldom more than three to the pod. They are sometimes roasted and eaten by children. The dried kernels contain from 25 to 27 per cent of a thick pale yellow oil, the composition, uses and value of which are at present but little known. It has been suggested that the whole seed might, if ground fine, to be fed to stock in India in a mixture with one of the cheaper pulses of the country and that, in the event of the oil being extracted, the residual cake might be used as a manure.

THE PLANT.

A NOVEL VACUUM DYEING MACHINE.

By FRANK C. PERKINS.

The accompanying illustration shows a new type of vacuum dyeing machine which is said to be a most satisfactory device for bleaching and sulphur black dyeing, also for hydrosulphate cold vat colors which have to be dyed at a low temperature.

It is pointed out that one of the principal difficulties in dyeing loose stock is the rolling and matting of the material into lumps, which seriously impairs the spinning qualities of the fibre. The only complete remedy is to color the material without agitating it, and this is accomplished by pumping the boiling liquor through the mass of stock which prevents any disarrangement of the fibres. By this means the material remains undisturbed during the dyeing process, and is removed from the tank in the same condition in which it was entered.

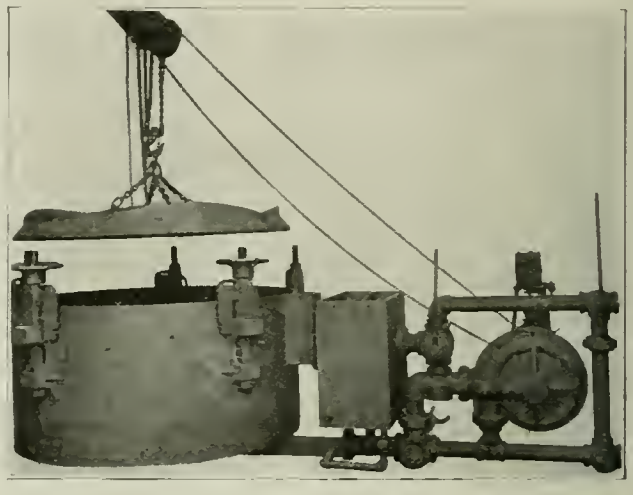
The new dyeing machine of the vacuum type combines the advantage of circulating process with an unusually convenient construction and efficient mechanical arrangement which reduces the cost of labor and dyestuffs to a minimum.

In the use of this apparatus a uniform temperature can be kept and in this way every fibre is subjected to the same treatment and the stock is colored an even shade, and the machine can be readily installed in the dyehouse on the floor level without any excavation.

When dyeing sulphur colors, where a standing bath is kept, the liquor after being used once is pumped to a storage tank, from which it is drawn for the next batch. The machine is very easily loaded and unloaded and after the stock is packed in the tank, the cover, which is supported on an overhead track, is placed in position, and as the liquor is forced through the stock, the cover settles down into place so that by a few turns of nuts it can be securely fastened.

When the batch is colored and rinsed, the cover is removed and the chain block hitched to the chain of the false bottom. The entire batch is then lifted from the tank and carried on the overhead track to the extractor, where it is dumped. The bottom is then placed in the tank ready for another batch.

It may be stated that the removing of the stock from the machine after dyeing is done by the engine which operates the device. There is attached to the main shaft of the pump a small pinion, which drives



New Type of Vacuum Dyeing Machine.

a gear wheel keyed on shaft and chain wheel, which is operated by an eccentric lever and when the machine is ready to unload, the hand chain of the block, which removes the load from the machine, is thrown into the sprocket wheel, and by running the engine this removes the load from the machine.

This gearing is so arranged that the load can be stopped at any point by throwing it out of gear, and can be lowered by the same means. This arrangement reduces the labor in handling the stock very materially, as the machine can be readily unloaded by a boy. The machine is adapted for cotton, wool, shoddy, rags and other loose material and hosiery.

All goods to be dyed, instead of passing through the liquor, as in the present method, can be dyed successfully by passing the liquor through the goods, which is much preferable, as it leaves the stock of whatever nature in perfect condition. It is claimed that these methods hardly can be appreciated unless the mill should have some of its stock dyed or bleached in this machine, and compared with goods dyed by other methods. This it is asserted at once demonstrated the advantages of the vacuum power. This new machine is a great improvement over the old type of dyeing machine, as it has great economy, capacity and durability and dyes one thousand pounds per batch.

It is held that there is a new field for this machine for bleaching raw cotton. It was generally maintained previously by carders that they could not successfully card cotton bleached in the raw stock by the old methods. When raw cotton is bleached by the

vacuum machine it does not affect the fibre in the least, as every operation, boiling, chemicking, souring and washing is done in the machine. The cotton is not rehandled and is so bleached that it cards just the same as ordinary cotton. In dyeing cold vat hydrosulphite indanthrene, Algol Ciba and Helidone colors, it is being used by mills which have obtained the government army contracts for dyeing their raw stock and the production of the machine is 20 per cent more than other circulating machines, also at less cost.

TURPENTINE EXPERIMENTS IN THE WEST.

In the rather elaborate formal report which the Forestry Division of the Department of Agriculture makes on the subject of the experiments into the utilization of Western pine for the production of commercial turpentine and other naval stores, a summary is given of the problems which confront the commercial development of this industry in the West.

The investigations that have been made thus far in the West, as has already been stated, cover areas in Arizona and California. The labor problems as well as issues arising with respect to transportation, etc., constitute the most important facts brought out in connection with the investigation.

The summary made by the experts of the department on these investigations induce them to state that "in considering the possibilities of commercial turpentine operations on Western pines, the problem of labor is one of the first that presents itself. In Arizona, Mexicans constitute a large part of the laboring class, but they are totally unfamiliar with turpentine work. Negro turpentine hands could be brought in from the Southeast, but their transportation would be costly. A few negro hands might be secured to teach the Mexicans, but whether the results would be satisfactory is, of course, unknown. In California both Indian and white labor is available in many timbered portions that have turpentine possibilities, here also the chippers would have to be taught how to use a hack.

The shorter season in Arizona, as compared with that of the Southeast, and the comparative severity of the winters in the timbered parts of the state might make it necessary to discontinue operations entirely for a few months during the winter. This would necessitate the reorganization of the operating force each spring, with a great many attendant difficulties. The California experiments were not started until June, so that the time when the gum begins to flow is not yet known. The flow continued in California longer than in Arizona. Temperature records taken on the California and the Arizona areas show a considerably higher average temperature in California. The diurnal range of temperature is greater in California than in Arizona.

Western yellow pine timber generally grows in open stands free from underbrush. In the majority of stands there would be but little, if any, more difficulty in moving the crude gum than in the Southeast. On rough ground burro pack trains might be used." Two small kegs or buckets holding about 150 pounds of dip could be slung on each animal.

The number of cups that can be hung on an acre of average Western yellow pine compares favorably with many areas that are now being turpentined in the Southeast. The Western trees are larger than most of the Southeastern ones. The bark of the Western pines is, however, thicker and rougher, and it will be necessary to remove the outer bark before hanging cups or chipping the trees; this, of course means the expense of an extra step not necessary in Southeastern operations. Such work can be done by the use of a broad ax or heavy spade-shaped tool with a cutting edge.

The cost of securing turpentine rights in the Southeast is constantly rising, and it is likely that turpentine stumpage could be leased at lower rates in the West.

At present the turpentine and rosin used in the West is shipped from the Gulf states. The advantage of cutting out a two or three thousand-mile haul to Western markets is evident.

The commercial success of turpentine operations in the Southwest will be doubtful until they have been tried on a commercial scale. Nearly as much turpentine and rosin was obtained from Western yellow pine, and the amount of timber available for turpentine operations in the Southeast is constantly diminishing. These two facts make it reasonable to suppose that turpentine operations in the large tracts of virgin pine timber of the West will in time be justified.

According to U. S. Consular Report American bituminous coal exports in the fiscal year 1912, were 14 7-10 million tons, worth 37½ million dollars, or over one-third more than in 1911.

The U. S. Consul at Mersina reports that heavy rains during June and July greatly affected the 1912 yield of Cappadocian gum tragacanth, and the output is estimated at 400 tons, against 500 tons in 1911. As most of the gum is discolored, the white qualities (which are the ones principally desired in the United States) are comparatively scarce and their prices somewhat high. Superior white gum is sold at 51 cts. per pound c. i. f. New York, extra white at 47 cts. and ordinary white at 41 cts. Yellow gums sell locally at 31 to 37 cts. per pound. About one-half of the yield of gum tragacanth is exported from Smyrna and Constantinople and the remainder from Mersina, shipments from the last-named port during the season 1911-12 amounting to 250 tons, valued at $180,000.

THE PRODUCTION OF CAUSTIC ALKALI AND BLEACH.*

By A. J. ALLMAND, D. SC.

The most important advances made in late years in the technical electrolysis of alkaline chlorides for the production of caustic alkali and chlorine are perhaps due to Dr. Jean Billiter, privatdozent in the University of Vienna. Some years back he designed a diaphragm cell which is being exploited by Siemens & Halske, and recently he has invented a modified form of the well known bell-jar cell, which is undoubtedly, taken all in all, one of the most efficient cells now operated technically. The Billiter-Siemens diaphragm cell I propose to mention briefly only, as full accounts of it are available elsewhere, and shall devote most attention to the Billiter "membrane" cell, the first installation of which started work early this year.

BILLITER-SIEMENS CELL.

Most diaphragm cells in technical use have vertical diaphragms (*e. g.,* Hargreaves-Bird, Townsend, Finlay). Billiter, however, has returned to the use of horizontal diaphragms such as were formerly employed by Le Sueur and by Carmichael. He has compared elsewhere the relative advantages and disadvantages of the vertical and horizontal arrangements.

A horizontal diaphragm is more slowly attacked chemically, as it remains more or less saturated with the alkali which migrates upwards from the cathode situated immediately underneath. This is particularly important when making strong alkaline liquors. Further, the hydrostatic pressure on it is uniform at all points, not varying with the height as in vertical diaphragms. This means a more uniform flow of liquid through, and consequently a more efficient checking of the movement of the OH ions towards the anode.

There are corresponding structural disadvantages. The floor-space needed is greater. Further, the insides of the cells are less easily accessible and the anodes are necessarily of more complicated construction.

The active diaphragm material in the Billiter-Siemens cell consists of a mixture of asbestos wool and $BaSO_4$, spread out evenly on top of a sheet of woven asbestos cloth, which in its turn rests on the iron-wire net-work which constitutes the cathode. The function of the asbestos cloth is merely to support the $BaSO_4$ mixture and to prevent its being displaced by the lively hydrogen evolution. The cathode makes contact with the iron bottom of a trough, the sides of which are lined with cement, and the anode chamber is formed by a non-conducting bell-jar, which is securely cemented around the edges of the diaphragm. An important feature of the cell is the arrangement for heating the electrolyte by means of eathenware pipes through which hot liquids run, these being immersed in the brine at the top of the bell-jars.

Cells have been made carrying up to 3,000 amperes at a current density of 4 to 6 amp. per sq. dm. Working at 89 to 90 deg., 12 to 16 per cent NaOH or 18 to 20 per cent KOH can be made at a 95 per cent cathodic current efficiency, employing 3.5 volts.

An interesting laboratory study of the Billiter-Siemens cell has been recently published by Mühlaus. He finds that the $BaSO_4$ used for the diaphragm is best precipitated hot. No change of size of grain when in the hot liquors of the Billiter cell is then likely to take place, and a regular and uniform flow is thus assured.

The highest current density permissible is about 6 to 7 amp. per sq. dm.

Above this limit, disintegration sets in. Using 30 to 32 per cent brine at ordinary temperatures, the following figures were obtained:

Concentration of alkali.	Current efficiency, Per cent.
3n.	98-99
4n.	95-97
5n.	80-85
6n.	75

The chlorine gas fell in purity from 99.5 per cent to 92 per cent as the alkali concentration was increased. The oxygen produced exceeded the amount of CO_2. The solid caustic resulting contained considerable quantities of $NaClO_3$ if produced from liquors stronger than 4n. The best results on the whole were given when making 4n. NaOH at a current density of 4 amp. per sq. dm. Raising the working temperature to 70 to 80 deg. improved both energy efficiency and purity of alkali.

The Billiter-Siemens process is now operated as follows:

(a) In Aschersleben, Saxony, by the Kaliwerke Aschersleben A. G. Ten 2,000-ampere units.

(b) In Höchst, by the Farbwerke Höchst.

(c) In Brückl, Bosnia, by the Bosnische Elektrizitäts A. G. Sixty-four 2,500-ampere units.

(d) In Krumau, Bohemia, by Ignaz Spiro and Söhne. Thirty-two 500-ampere units.

(e) At Niagara Falls, by the Niagara Alkali Company. A 1,000-kw. installation of 3,000-ampere units.

A number of plants are also being installed or enlarged. The Niagara Alkali Company (which has succeeded the old Roberts Chemical Company), is at present increasing the size of its plant from 1,000 to 3,000 kw. It has also been made known that a new factory for caustic alkali and bleach is being erected, commencing with 78 2,000-ampere units, and that a textile factory is installing twenty-four 100-ampere units.

BILLITER-LEYKEM CELL.

In this cell Billiter has successfully modified the bell-jar process, placing the cathodes (hooded to collect the hydrogen) immediately *underneath* the bell-jar, and not around its sides, as in the Aussig cell. Similar constructions had been formerly sug-

*Paper read before the Faraday Society in London on November 26, 1912.

gested by Richardson and by Bein, but had achieved no technical success.

By doing this, Billiter gains an important advantage. In the ordinary bell-jar cell, both flow of liquid and flow of current change in direction at the lower edge of the bell-jar. This results in non-uniformity of current density and liquid flow in the different parts of the bell-jar section. At some points liquid will be flowing more quickly than is necessary to overcome the OH′ migration towards the anode, at

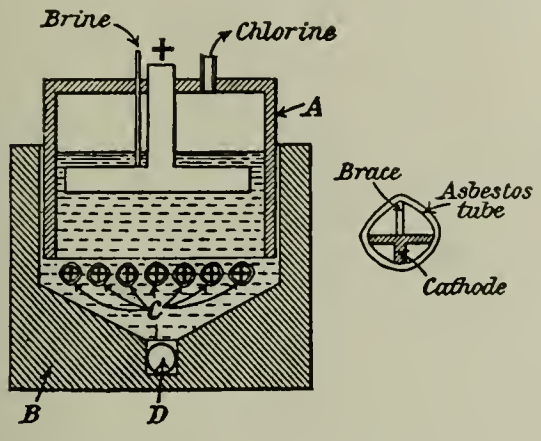


Fig.1—Section of Billiter—Leykam Cell.

other points the contrary will be true; the movement of the OH′ ions will predominate, and the current efficiency will fall. This last statement particularly holds for those parts of the bell-jar section furthest removed from the walls, where the current of liquid is exceedingly slow. The larger the bell-par, the greater proportionately is this disturbance. It also increases rapidly with current density. The consequence is that the units (bell-jars) at Aussig are very small, and can only be worked at a low current density, furnishing weak alkali. Such a plant requires much floor space for its output and the labor charges are high.

In the Billiter cell, this change of direction and the resulting irregularities are avoided, the motion of the brine being directly opposed to that of the current lines until it has passed the cathodes. The consequence is that high current densities can be used, stronger caustic liquors produced, high current efficiencies obtained, and large units constructed. At the same time, the advantage of the bell-jar cell—the absence of diaphragms—is essentially retained. For, though the *current* must all pass through the hoods which cover the cathodes, this is not true of the electrolyte. Most of it passes directly through the spaces between neighboring cathodes, and is charged with caustic by diffusion from the concentrated alkali which fills the cathode hoods. Not only does this alkali protect the hood material (in practice, woven asbestos) against chemical action of chlorine compounds, but suspended matter present in the brine is not filtered out, as happens in diaphragm cells, and it is not necessary to purify the brine in any way. The asbestos hoods are made of as coarse a structure as is consistent with their function of leading off the hydrogen gas, and affect the voltage to a very slight degree only. Finally, the cell is heated in a similar fashion to the Billiter-Siemens cell, and the voltage thus lowered.

The essential parts of the Billiter-Leykam cell are shown diagrammatically in Figs. 1 and 2. A is the bell-jar inverted in the cement trough B, and provided with anode outlet for chlorine, inlet for brine and heating arrangement. The cathodes C are arranged below the bottom level of A and consist in practice of T-iron. They are enclosed separately in long woven asbestos tubes which are suitably braced in order to avoid deformation by the evolved hydrogen, and are slanted sufficiently to allow the gas to stream away readily. These cathodes project out into a side compartment of the cell as shown, from which the hydrogen can, if necessary, be collected.

The causticized brine flows off through D.

The Austrian rights to the Billiter bell-jar cell have been purchased by the paper manufacturers Leykam-Josefsthal A. G. The first plant has been erected in their mill at Gratwein, a village on the Austrian Southern Railway, a few miles from Graz, has been in continued operation since early 1912, and has given every satisfaction. Some 1,700 to 1,800 kilos of active chlorine are produced daily, and the whole plant uses about 400 P. S.—350 P. S. for the cells and 50 P. S. for auxiliary pumps, fan, etc. Power is purchased from a company at 150 kr. ($31.25) per P. S. year. After converting into direct current, and reck-

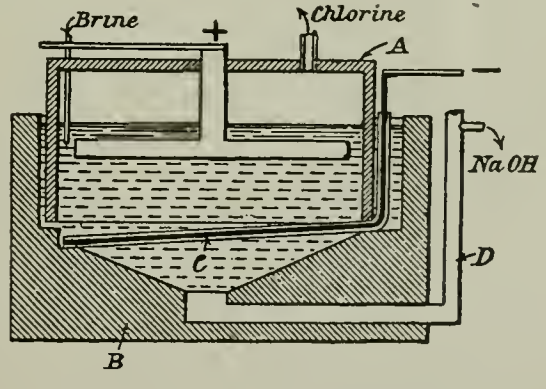


Fig. 2—Section of Billiter—Leykam Cell.

oning all losses in leads, etc., the cost comes to 180 kr. ($37.50) per P. S. year.

The plant consists of 561,200-ampere units, 50 of which were working at the time of my visit last July.

The cells are 5.5 meters long, 1.1 meters broad (internal measurements), and about 1.3 meters high. The side walls commence to slope inwards about 70 cm. below the top of the cell. They are built of reinforced concrete, the upper part being lined with earthenware bricks set in cement.

They are provided with three cement lids, each of which carries eight anodes.

The anodes are of Acheson graphite (1.0 × 0.18 × 0.05 meter), each being led through its lead by means of two graphite rods. The lids are cemented on to a shallow shelf cut out of the wall of the cell by means of ordinary putty, which stands the action of chlorine very well and always remains fairly soft. Putty is also used at the points where the anodes pass through the lids, as the weight of the anodes is not borne by the latter, but by the copper leads above. Each anode takes 50 amperes at a current density, assuming lower and side surfaces to be active, of about 1.6-1.7 amp. per sq. dm.

The cathodes are of T-iron and enclosed in woven asbestos tubes. These taper down slightly towards their closed lower ends, and the whole is braced by the insertion of a wedge-shaped strip of asbestos cement. The tubes pass through holes in the dividing wall into the side compartment of the cell as indicated in Fig. 1. Two iron rods attached to each T-iron cathode take the current to the copper leads above. The hydrogen is allowed to escape. The cathodes are, of course, about 1 meter in length, and the mean breadth of the asbestos tubes is about 5 cm. Between each tube there is a space of 5 to 8 mm. The upward slope of these tubes is about 2 cm. per meter.

The brine (moving from a reservoir under gravity) is led to a distributing box situated above the cells. From this it proceeds by way of a series of short capillary tubes (1.5 mm. bore) to 22-in. tubes, which pass through the cell lids, and is thus fed in between the anodes. Regulation of the main supply to the cell is effected by means of a rubber tube and clip. This arrangement acts on the whole very satisfactorily, though the capillaries sometimes get stopped up. The causticized brine is drawn off from one side of the cell by means of siphon overflows. Three are provided, but one only is used in practice.

The heating arrangement used by Dr. Billiter in his diaphragm cell, though available for all other installations of his "membrane" cell, cannot be used at Gratwein. (The patent rights are not there available). The cells are, therefore, provided with a heating arrangement which employs steam, the details of which however, I cannot divulge here. When I was at Gratwein, the cells were being mostly worked at room temperature, whilst those few which were being heated were working at 65 deg. to 70 deg. C.

The cells are arranged in four rows, two rows being worked in series, and are insulated by glass resting on concrete supports. Beneath the cells are arranged the chlorine and brine pipes, and a channel for the caustic liquors. The chlorine pipe-line is constructed of cement, junctions being made by covering the ends with a cement box and filling up with asphalt. The current leads are of copper, those connecting the cells of circular cross-section and 3 cm. in diameter. They are all painted with a composition stable against chlorine and acid fumes, as are also the tin tubes and rubber connections referred to above. The cells are worked under slightly reduced pressure (½ cm. of water), and, as a matter of fact, no smell of chlorine was noticeable. Ventilation can be effected, if necessary, by blowing air in through the agency of a fan driven by a horsepower motor. A traveling-crane is provided to facilitate lifting off the tops of cells, etc.

Saturated brine is used, prepared in the simplest way. A long cement trough is filled with large lumps (20 to 40 cm.) of crude salt. Waters enters continuously at one end, and saturated brine leaves at the other. It is not purified, and can be sent straight to the cells. The average cathode liquors produced contain 12 to 13 per cent NaOH and about 20 per cent NaCl. By decreasing the rate of flow of brine, 16 per cent NaOH can readily be made. Up to 350 liters of brine per cell are causticized in 24 hours. The liquors are first evaporated in two vacuum pans, furnished by the Skodawerke A. G., Pilsen, and similar to those used in sugar refineries. In these they are successively brought to 30 deg. and 40 deg. B. Then by means of a Kaufmann rapid evaporator they are brought to 50 deg. B, before going to the melting-house. The final product, which will probably be later somewhat improved upon, contains 97 per cent NaOH, 1.2 per cent Na_2CO_3, and 1.8 per cent NaCl. The chlorine is diluted and absorbed in milk of lime.

Cells which are worked at room temperature take about 4 volts. Those I saw working at 65 to 70 deg. require 3.4 to 3.5 volts. Long continued experiments carried out with a 250-ampere unit have shown that at the normal working temperature of 85 deg. the voltage falls to 3.1 volts (*plus* in all cases the voltage drop in the leads). The cathodic current efficiency is about 92 per cent for 3n to 4n alkali.

It remains to be added that wear and tear in the cells are very small. Under normal working conditions the anodes lose about 1 mm. in thickness at their bottoms and sides in two months. Suspended matter in the brine settles on the bottom of the cells, and the asbestos hoods remain unaffected. Finally, when once matters are adjusted, the whole system works automatically. The actual cell-room in Gratwein is worked by shifts of one workman only, whose duty it is to adjust the rates of flow in the different cells. Moderate fluctuations in rate of flow of brine or in current density result in a change in the alkalinity of the liquors produced, and in a corresponding *small* change in current efficiency. The cells at Gratwein work at a current density between the electrodes of about 2 amp. per sq. dm. only. With cells working at 85 deg. the most convenient figure, according to Billiter, is 4 to 6 amp. per sq. dm.; but, by suitably varying the other conditions, 14 amp. per sq. dm can be employed.

The withdrawal of 350 liters of catholyte per cell per 24 hours corresponds to a movement of the brine of about 0.00007 cm. per second. The OH ions in that part of the catholyte between the electrodes will

have a velocity anodewards of just about the same magnitude. (*E. g.*, assuming the cell to work at room temperature, the conductivity of the electrolyte would be about 0.5 recip. ohm per cu. cm., the velocity of the OH ion at a voltage gradient of 1 volt per cm., 0.0018 cm. per sec., and the actual velocity $0.02 \times 0.0018 \div 0.05 = 0.000072$ cm. per sec.). This close approximation between the two opposing velocities, with the consequent straying of OH ions towards the anode, is of course the chief cause of the 8 per cent deficiency in current efficiency, as the amount of chlorine which dissolves in the concentrated brine, and which would thus tend to be carried to the cathode, is very small.

In conclusion, I will again emphasize the chief characteristics of the Billiter-Leykam cell. They are—

(1) Freedom from diaphragm troubles.

(2) Use of impure brine.

(3) Automatic working, great adaptability, and low attendance charges.

(4) Alkali (3n to 4n) strong compared with most other non-mercury cells.

(5) With heated cells, lowest energy consumption per ton of product of any of the electrolytic cells now working on a large scale.

OIL AND GAS IN OKLAHOMA.

In the early part of 1912 Robert H. Wood, of the U. S. Geological Survey, made an investigation of the oil and gas developments in north-central Oklahoma, visiting localities where producing wells and test holes had been sunk. His report has just been issued by the Survey as Bulletin 531B, a copy of which may be obtained on application to the Director of the Survey at Washington, D. C. In addition to collecting well data, Mr. Wood made some observations on the structure and character of the formations exposed at the surface. Nearly all the information concerning the wells was furnished either by oil companies or by local citizens. The region included in the report comprises lands formerly within the Pawnee, Otoe, Ponca, Kaw, and Tonkawa Indian reservations. The principal towns within the area are Guthrie, Pawnee, Perry, Ponca, Newkirk, and Blackwell.

Oil has been known east of these reservations, in the Cherokee and Creek nations, since the late eighties. Development started in the vicinity of Alluwe, Bartlesville, and Muskogee in the early nineties, but little was done until the early part of the last decade. In 1906 the famous Glenn pool, near Sapulpa, was discovered and it has proved to be a phenomenal producer. Encouraged by results obtained in these fields prospectors soon began drilling farther west and in the region embracing the five Indian reservations mentioned. Foreign capitalists have sunk a number of holes in widely separated localities, and many local companies have drilled in an effort to reach oil or gas.

DISCOVERIES OF PHOSPHATE DEPOSITS.

From outcrops of phosphate rock in the Garnet Range, six miles north of Garrison, Mont., may be seen, 35 miles away, immense volumes of smoke pouring out of the smelter stacks at Anaconda—great quantities of sulphurous acid escaping into the atmosphere. At times this acid-laden smoke clouds the whole Deer Lodge Valley. The great economic importance of this situation lies in the fact that phosphate rock is quickly rendered available as a plant food by dissolution in sulphuric acid. The combination of immense deposits of phosphate rock and a practically unlimited and readily accessible supply of sulphuric acid may have considerable bearing on the agricultural progress of the West in years to come, if not indeed at present.

This deposit of phosphate near Garrison is one of three discovered in Montana in 1911 by J. T. Pardee, of the U. S. Geological Survey. The others are at Philipsburg, on the south slope of Flagstaff Hill, and half a mile east of Elliston, north of Little Blackfoot River. Rock phosphate was also discovered in the same year by R. W. Stone, of the Geological Survey, about two miles east of Cardwell, Mont., on the Northern Pacific Railway, at the summit of the cliffy slope rising to the west from Jefferson River.

These discoveries were merely incidental to the prosecution of other geologic work, so that the deposits were not studied in any great detail. Enough was learned, however, to make certain that they are commercially valuable and of the same type as the phosphate found by Hoyt S. Gale, also of the Federal Survey, near Melrose, Mont., in 1910 and that of the extensive Idaho-Wyoming field. The deposits discovered by Mr. Pardee lie from 60 to 70 miles north and that by Mr. Stone 40 miles northeast of Melrose; hence they may be said to extend the limits of the known phosphate field for those distances.

At the point near Garrison the phosphate bed is 8 feet thick and more than 4 feet of it is shown by analysis to be high-grade material. At neither Philipsburg nor Elliston was the thickness of the bed determined, but the outcrops show that in each place it is at least a foot thick and the distribution of float indicates that it is probably more, about the same as in the Garnet Range. At Cardwell it probably exceeds 2 feet in thickness.

Although detailed work on which to base a tonnage estimate has not yet been done, it is apparent from the examinations made that in the Garnet Range, at least, a large amount of phosphate is present. For instance, 14,000 tons would be the content of an acre underlain by a flat bed of phosphate 4 feet thick. Where the phosphate bed is steeply tilted, as it commonly is in this region, the amount beneath an acre is much greater.

METALLURGY

EXPERIMENTS WITH OPEN HEARTH REGENERATORS.

In the issues of Stahl und Eisen for Oct. 4 and Nov. 7 is a very interesting paper on open hearth regenerators by E. Juon, steel works superintendent of the Donez-Jurjewka plant, South Russia. It is abstracted as follows in *The Iron Age*.

The chief duty of the regenerator, as the name implies, is to accumulate heat from the waste gases in the bricks of the checker work. This is not all, however, for above everything else it is part of the system through which the gases are led to or from the hearth, and must allow free passage to these gases. These requirements are altogether separate and conflicting. Every furnace manager is taught early in his career that the heat efficiency of his checker work will be greater the smaller the spaces between the bricks, and the more tortuous the passages between them. Checker work with bricks laid in complicated ways has been tried many times, but without success because such an arrangement greatly hinders the passage of the gases. In any discussion of regenerators the uptakes which lead the gas and air to the ports, and through them to the furnace, must also be considered.

Details of the Tests.—Below are collected some observations with reference to these requirements. In the course of the furnace run the conditions affecting the regenerators change very considerably. Their efficiency continually grows less until, if no other reason intervenes, the furnace has to be shut down.

The tests carried out at the open hearth plant of the Donez-Jurjewka Company covered a considerable period of time. The plant consisted of five furnaces of 30 to 35 tons capacity, and one furnace of 45 to 50 tons. The output of ingots in 1911 was over 220,000 metric tons (2204.6 lb.). A seventh furnace of 60 tons' capacity was started in March, 1912. All the furnaces work exclusively with a liquid charge. Their capacity was gradually increased from 22 to 35 tons without the regenerators being made correspondingly larger. The latter are therefore heavily overloaded so that they require continued careful attention. A systematic investigation must be carried out along two lines; namely, the temperature and the pressure conditions, or the pressure in different parts of the furnace system. The temperatures were carefully taken many times in the day in each of the positions chosen, but unfortunately no instruments were available by which an uninterrupted continuous record could be obtained. The Wanner pyrometer was used, and some special red glasses were previously carefully standardized by the pyrometer.

The Taking of Pressure Records.—The pressures were taken by the positive and negative pressure meters manufactured by the Hydro apparatus company of Düsseldorf. They give a continuous record and five of them were available. The smallest change in pressure is indicated, so that the records serve to show the whole operation of the particular furnace under investigation. Not only the reversals of gas and air, but the work of the gas producers, such as poking and cleaning, are clearly indicated, as well as any change in the valves, the charging, the reaction of the bath in the furnace, and the tapping of the heat.

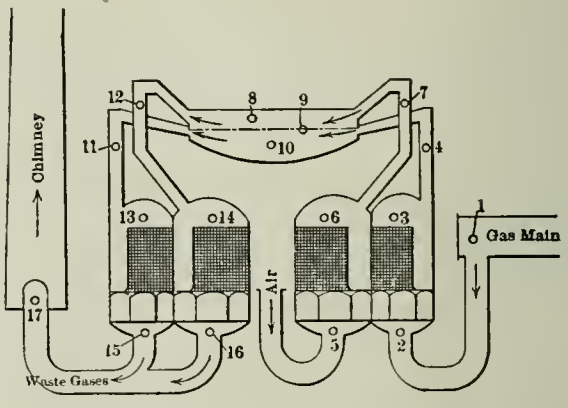


Fig. 1—Position for Taking Pressure Record.

The meters were at first installed as a control apparatus, for which they are well fitted. Little consideration was given originally to the actual pressure values, as no positive connection could be determined between them and the furnace operation. Under normal conditions the daily pressure records taken at the same place in the furnace system look almost alike. Over 3,000 such records were taken during the last two years and carefully compared. A record showing abnormal conditions can now be separated from a normal one at the first glance. Records of normal conditions are used below unless otherwise stated. By such conditions are meant those obtaining during the period between the 20th and 500th heat, with a temperature of about 1,200 deg. C. in the upper part of the regenerators, with correct gas producer operation and wide open valves.

Table I shows the positions where the pressure records were taken. Those in the hearth could not be measured by the instruments, and an ordinary U tube was used. Fig. 1 shows the positions diagrammatically. The normal values for pressure and tempera-

ture are given in Table I, together with the density of the gases calculated from their analyses and the area of cross-section of the particular places. Some of the pressure records given in the original paper are reproduced below:

TABLE I.—POSITIONS OF PRESSURE METERS, WITH AVERAGE PRESSURE AND TEMPERATURE.

No.	Positions.	Average pressure mm. water.	Average temperature deg. C.	Density of gases, deg. C and 760 mm. Air = 1.	Area of cross section, sq. in.
	Gas—				
1	In the gas main...	+15	600	0.90 to 0.94	1209
2	Gas flue, under gas regenerator	(+2 to +11) +5	(650 to 750) 700	0.92	1395
3	Top of the gas regenerator		(1100 to 1300)	0.92	7750
4	Uptake above gas regenerator	+4 (+5 to +10) +7	1200 (1200 to 1300) 1250	0.92	465
	Air—				
5	Air flue under air regenerator	—1	(400 to 700) 550	1.00	1937
6	Top of the air regenerator	±0	(1100 to 1350) 1225	1.00	9610
7	Vertical uptake above air regenerator hearth.	+3	(1250 to 1400) 1300	1.66	465
8	Above center line..	Small pressure	Up to 1800		
9	Center line	±0	Up to 1800		
10	Below center line...	Small pressure	Up to 1800		
	Waste Gases—				
11	Vertical gas downtake	(—2 to —3) —3	1700	1.01 to 1.05	465
12	Vertical air downtake	+1.5	1700	1.03	465
13	Top of gas regenerator	—14 to —15	1600	1.03	7750
14	Top of air regenerator	—14 to —15	1600	1.03	9610
15	Below the gas regenerator	—19	750	1.03	1395
16	Below the air regenerator	—18	700	1.03	1937
17	Base of chimney stack	—33	600	1.03	1550

NOTE.—The pressures are given in mm. water to agree with the records reproduced (1 mm. water = 0.0394 in.).

The work of the regenerators deteriorates each hour in the short periods between the reversals of gas and air. This is shown, for instance, in Fig. 2, which gives the record taken at the lower part of the air regenerator. The exhaustion is the greatest immediately after reversal, and gradually decreases until the next reversal. This is not only the case when directly connected to the stack, but also when connected to the furnace. However, the changes in the latter period are much smaller, about 0.2 mm. water between reversals, while in the former case they are about 2 mm. This is clearly shown at A, B, A_1 B_1, etc., in Fig. 2. These regular periodic changes naturally depend on the changes in temperature, and are always more noticeable toward the beginning of the furnace run than toward the end. It appears as if they were due to the checker work being clean and not covered with slag, and so being a better heat conductor. Fig. 2 was taken at the beginning of the run, heats 30 to 34.

Conditions Affecting Movement of Gases.—Two conditions affect the movement of the gases in the regenerators. The first is the tendency to rise which increases with increasing temperature, and the second is the frictional resistance of the brick work which also increases as the temperature rises. If the regenerators are directly connected with the stack then a constant increase in temperature takes place between reversals. This brings about increased resistance and also greatly increases the rising tendency of the waste gases, which in this case acts as resistance. The draft, therefore, is decreased by the sum of these two resistances. If the checkers are connected to the hearth then a continuous decrease in temperature takes place. The internal resistance slowly grows less, and also the tendency to rise, which in this case works positively. The draft, therefore, only decreases a very little, according to the continuous difference between these two forces. These conditions are clearly seen in the pressure records.

The records taken at the base of the chimney also

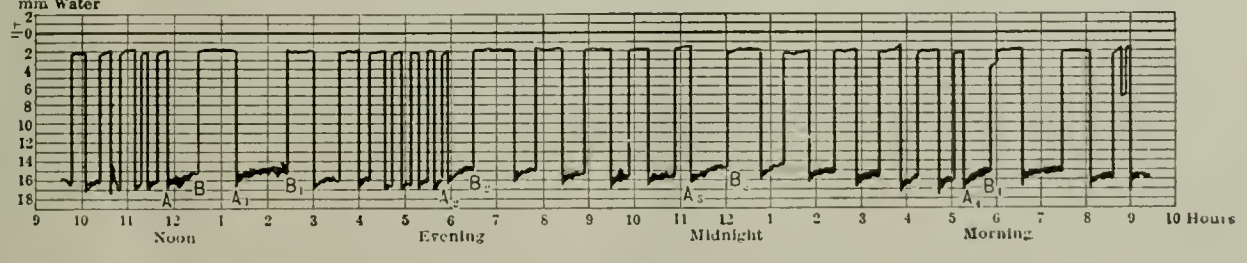


Fig. 2—Deterioration of Regenerators Between Separate Reversals.

The records for the various positions are characteristic and allow the real average values to be obtained for the separate working periods, which is impossible with the ordinary methods of pressure measurement. The main purpose of these records is to give a clear idea as to whether everything is working properly; if not, the reason must be indicated so that the proper remedy can be applied.

show the changes due to temperature differences between reversals. They also show other periodic changes occurring at longer time intervals, namely, the lowest draft pressures which are reached from 1½ to 2 hours after the tapping time, and during charging. A record taken at the same time in the air regenerator shows that this period also corresponds to that of greatest time intervals between reversals.

How Symptoms of Deterioration Show.—The slowly increasing deterioration of the checkers during the furnace run is the most fatal to the furnace. The burning back of the ports is often the cause of shuting down the furnace. Attempts are now being made to obviate this by the use of water cooled ports, changeable ports, and other special arrangements. Even with completely good ports, however, there finally comes a time when the furnace shows clear signs of age. An ordinary furnace working with cold charges should run for somewhat more than 1,000 heats. The life of a large furnace with liquid charges is shorter. At Donez-Jurjewka various operating troubles become evident after 500 heats, and more than 750 is only reached in exceptional cases. The symptoms of weakness due to age are an increase in coal consumption, then the flame development in the hearth becomes bad, metal is left around the edges of the bath after tapping, there is not air enough, the checkers are not uniformly hot, the time of the heat is very long, the heats are dead and cold, notwithstanding the increased coal consumption, etc.

All these appearances are due, in the first place, to bad working of the regenerators as part of the furnace system. If two pressure records taken in the regenerators at the beginning and end of a furnace run are compared, the difference is seen at once. (Figs. 3 and 4, taken underneath the checker work). The draft when connected with the stack, and the pressure when connected with the furnace have increased from 1½ to 5 times. The case in the upper part of the regenerators is exactly the opposite. There the records show that with an old furnace the pressure on the ingoing end and the draft on the outgoing end have decreased compared with conditions at the beginning of the furnace run. The records show that while the pressure in the lower part of the regenerators has increased from ¾ mm. to 15, 17 mm. in the upper part it has fallen from 3 mm. to 0. This is the most striking expression of the influence of the age of the furnace on the movement of the gases through the furnace system, as shown by the pressure records.

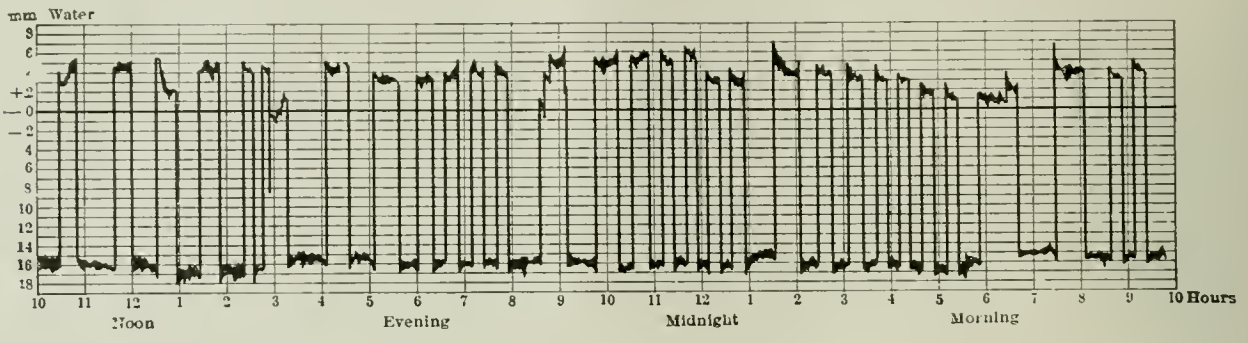


Fig. 3—Pressure Record from Underneath Gas Regenerator, After Heat 156.

Measuring Resistance to Gases.—If other positions are investigated in connection with the age of the furnace, it is found that all in front of the checkers show striking increase in pressure while all behind show a decrease. Briefly it is clear that it is the regenerators which have suffered the greatest change due to age. The resistance offered by them to the passage of the gases has been strikingly increased. This can only be based on the two conditions mentioned before, and it is evident that the increase in the frictional resistance is the chief cause since the tendency of the gases to rise cannot be greatly different because the size

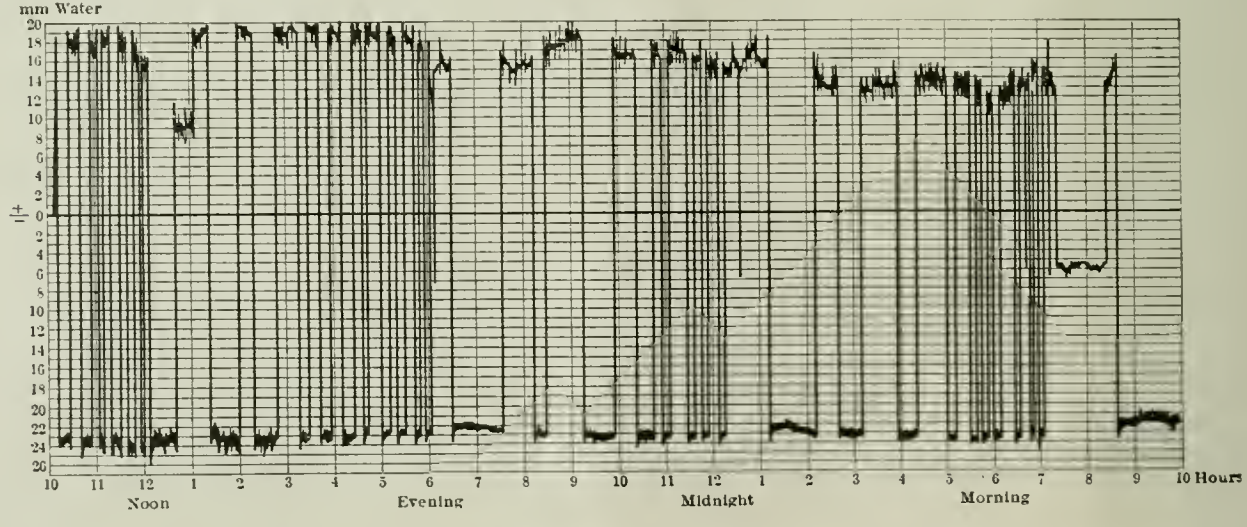


Fig. 4—Pressure Record from Sane Position as Fig. 3, After Heat 607.

of the chambers and the temperatures are not greatly altered during the furnace run. This increased frictional resistance is easily explained by the accumulation of dust in the checker work, and the slagging of the bricks. The value of the pressure records at this state of the furnace run is that through a comparison of those taken above and below the regenerators, the amount of resistance which they offer can be determined, and also the amount of slagging in each separate chamber.

The first one to see the bad effects of this increased resistance is the first helper or melter. The gas enters the furnace without force and a good flame cannot be produced. He then complains of lack of gas or bad gas. This makes the producer man work harder, he pokes with increased energy, uses more coal, and where it is possible increases the blast on the producer. At first this helps, for the increased pressure rule is above the gas port. All these make the tendency to rise and the resistance offered more favorable than in the case of the gas. Notwithstanding, the time comes when the passage of air is greatly hindered for the same reasons mentioned in the case of the gas. This causes a lack of air in the furnace. Then if the gas pressure is purposely increased there is very quickly incomplete combustion, unless the air supply was previously very plentiful (which naturally is bad in itself) and this causes the furnace to work cold and markedly reduces the output.

Analyses Showing Lack of Air.—An analysis of the waste gases will generally prove a lack of air, but only carefully taken average results must be used. Such tests taken from a series of analyses are given in Table III, the composition of the producer gas being approximately the same during the two periods. The test samples must be taken with the furnace doors

TABLE II.—AGE OF FURNACE AND COAL CONSUMPTION.

Date, 1910.	No. of heat in series.	No. of heats.	Average time of heat, hours (see note).	Production of ingots, tons.	Coal consumption per day, tons.	Coal consumption per 100 tons ingots, daily tons.	Coal consumption per 100 tons ingots, average tons.	Coal consumption per production hour (see note), daily tons.	Coal consumption per production hour (see note), average tons.	Average gas pressure in regenerators, lower part, mm.	Average gas pressure in regenerators, upper part, water.
June 19.....	156-59	4	4.7	130.5	26.6	20.3		1.11		+6	+5
June 20.....	160-64	5	4.5	165.0	29.1	17.6		1.21		+5	+5
June 21.....	165-68	4	5.0	135.0	28.1	20.8	19.07	1.17	1.14	+4	+4
June 22.....	169-72	4	4.7	133.3	26.8	20.0		1.11		+4	+4
June 23.....	173-76	4	4.9	141.5	26.6	18.8		1.11		+5	+4
June 24.....	177-81	5	4.8	160.0	27.9	17.4		1.17		+4	+3
Oct. 23.....	600-02	3	5.6	96.6	30.0	31.0		1.25		+18	0
Oct. 24.....	603-06	4	5.7	131.6	30.6	23.2		1.27		+18	+1
Oct. 25.....	607-10	4	5.8	135.0	29.6	21.9	24.61	1.27	1.26	+17	0
Oct. 26.....	611-13	3	5.8	102.5	28.3	27.6		1.18		+16	0
Oct. 27.....	614-17	4	5.7	132.9	30.8	23.1		1.29		+17	0
Oct. 28.....	618-21	4	5.7	136.6	31.6	23.1		1.32		+16	+1

Notes.—45 minutes is allowed between heats for making up bottom, etc. This is not included in the time of heat. The day is calculated as having 24 production hours.

at which the gas enters the regenerators equalizes the increased resistance; but it is a very expensive way of improving the flame development. As soon as the pressure records, with otherwise normal conditions, give evidence of slagging in the regenerators, then the coal consumption begins to increase, both per unit of production and of time. This is shown in Table II, giving the fuel consumption at periods corresponding to Figs. 3 and 4.

It should be particularly emphasized that these two working periods were not chosen specially for comparison, but that such periods are to be found in every furnace run.

Although the decrease in the working capacity of the gas regenerators can be partly remedied by an increase in the gas pressure, this does not apply to the air, so that the same appearance in the air regenerators is much more harmful for the furnace. At Donez-Jurjewka the latter are usually kept 50 to 100 deg. C. hotter than those for the gas. The uptakes are continued higher above the checkers and the air port as a

TABLE III.—CHIMNEY GAS ANALYSIS.

	Date 1910			
	June 21-22	June 26-27	October 25-26	October 27-30
Age of furnace by heats...	165-172	185-193	607-613	625-631
Per cent by Vol. CO_2	10.2	9.1	16.1	14.2
O	7.7	8.4	3.9	3.1
CO	...	...	0.2	0.4
N	82.1	82.5	79.5	82.3
Excess coefficient for air: $\text{Excess} = \frac{N}{N - 79\frac{O}{21}}$	1.54	1.62	1.22	1.16

properly closed, otherwise much air is drawn in and the analyses will be incorrect. How harmful an excess of air drawn through the doors is for the furnace need not be mentioned. With old furnaces the combustion is often so incomplete that at night it is evidence by the flames from the furnace stacks.

Hand in hand with the lack of air, which moreover cannot always be clearly proved and is often unjustly blamed for many things, there is ununiformity in the heating of the air regenerators. At Donez-Jurjewka

the furnaces are built on the eight regenerator system, and each of the chambers was carefully investigated. In Table IV a remarkable case of bad heat distribution is given. The temperatures were measured in the upper third of the regenerators on heat 643 of furnace No. 3, one day before it was shut down.

TABLE IV.—COMPARISON OF REGENERATOR TEMPERATURES IN OLD FURNACE JUST SHUT DOWN.

Positions.	6 A. M. Gas from left to right, deg. C.	12 M. Gas from right to left, deg. C.	2:30 P. M. Furnace is charged, deg. C.	8 P. M. Before tapping, deg. C.
Front gas regenerator right..	1105	1080	1005	1096
Back gas regenerator right...	1190	1160	1105	1177
Front gas regenerator left...	1043	1080	975	1055
Back gas regenerator left....	1055	1080	950	1055
Front air regenerator right...	1100	1190	1190	1266
Back air regenerator right...	1009	975	900	900
Front air regenerator left....	1080	1096	1055	1080
Back air regenerator left.....	1055	1055	1080	1096

In such cases changing the valves does not help any more. The whole behavior of the air checkers shows such irregularities as can only be explained by a complete slagging of a certain part of the checker work. It appears, for example, that the cooling of certain parts increases after reversing instead of increasing. While an outside gas pressure assists the passage of gas through the checker work and uptakes, the air regenerator has no such outside assistance at its disposal, the only help being the rising tendency of the gas in the chambers and uptakes above. If the pressure records of the air and gas regenerators are compared, there is seen to be a difference. In the case of the gas it is only after the stream has passed along the whole way and entered the hearth that the pressure drops to that of the atmosphere. In the case of the air, however, the first equalization with this pressure is reached in the upper part of the regenerators. A positive pressure is then produced in the vertical uptakes, and in the hearth it is again equalized.

Good Results With Blast From Fans.—The air supply system may be compared to two pumps. One is signified by the checker work of the regenerators. It pulls the air from outside and delivers it under the roof of the regenerators at the original pressure. It could not proceed further unless it came at that point under the influence of the second pump that is situated in the uptakes and supplies the air direct to the hearth. In each space designated as a pump the positive force consists of the tendency of the heated air to rise, the negative of the frictional resistance. As the latter constantly increases with the age of the furnace the time comes when the checkers are in such condition that the former cannot overcome it. The influence of the uptake then tries to bring about a vacuum in the upper part of the regenerator, finds this difficult, and the amount of air supplied to the hearth is greatly decreased. These conditions then lead to incomplete combustion. Just as we have the possibility in a similar case of increasing the outside pressure and forcing gas through the gas regenerators, so there is here the same possibility of forcing air through the chambers by outside pressure. This has been pointed out by Dichmann and others.

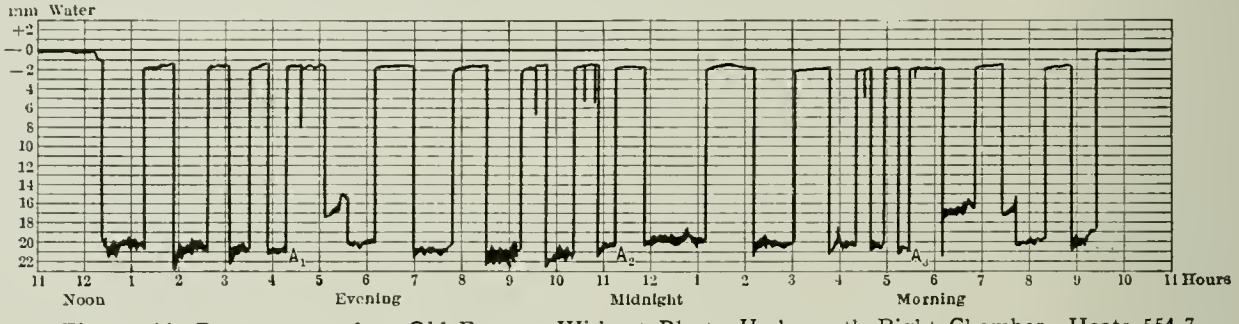


Fig. 5—Air Regenerator of an Old Furnace Without Blast—Underneath Right Chamber—Heats 554-7.

It was thought, therefore, that the time was ripee to try this at Donez-Jurjewka, using as a basis the many pressure records, and experiment with an old badly running furnace. Accordingly a fan was provided and tried out at the proper time. The results exceeded expectations. The fan is 635 mm. (25 in.) diameter and driven by a 3-5-hp. motor at a velocity of 500 r. p. m. The amount of air furnished is 260 cu. m. (9.182 cu. ft.) per second, with a pressure of 25 mm. of water. The driving motor can be switched on and off by the melter from the working floor. As the speed of the motor cannot be changed, a simple valve arrangement is used, so that the excess air can escape and only the amount needed be used. After the proper conditions of working had been determined by means of analysis, pressure records and tempera-

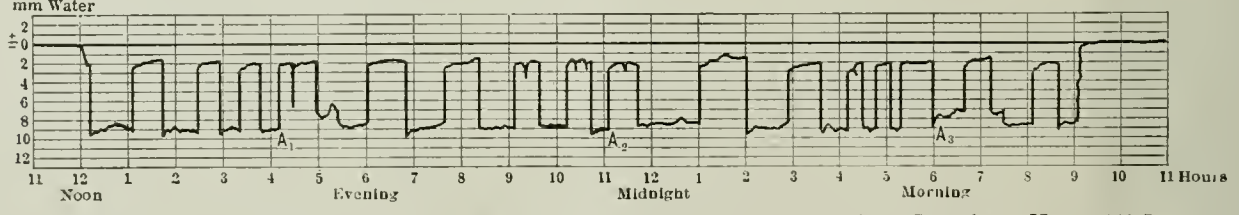


Fig. 6—Air Regenerator of an Old Furnace Without Blast—Above Right Chamber—Heats 554-7.

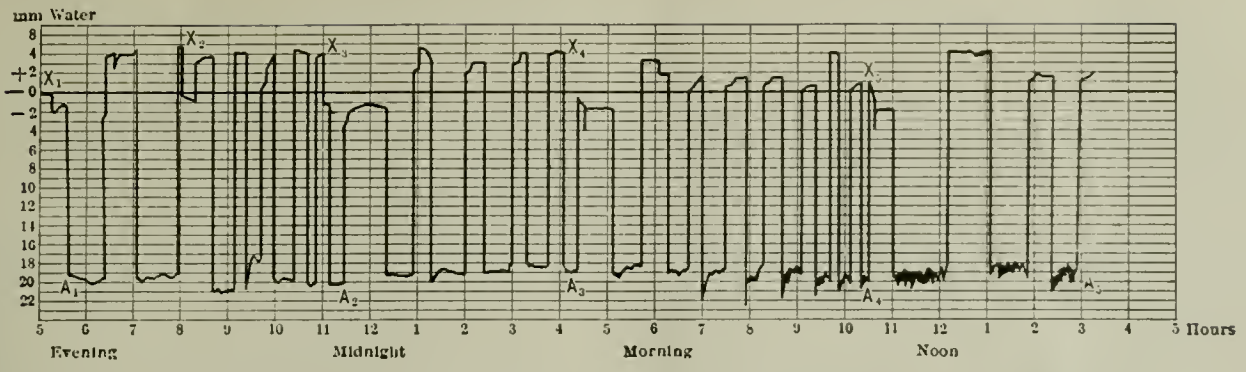


Fig. 7—Air Regenerator of an Old Furnace with Blast—Same Position as Fig. 5—Heats 574-8.

tures, the blast was available, and is now always used at the end of the ordinary furnace run, if there is proof of obstruction in the regenerators. Usually the blast is started after the heat is charged and not changed until shortly before tapping. The first day, even with a mild blast, it generally makes the flame blow strongly out of the doors. This, however, soon stops in a most astonishing way. It appears as if the increased pressure of the waste gases, which cannot at first penetrate the checker work, gradually breaks its way through. Perhaps the increase in temperature plays a part and melts down the solid slag deposits resting on the upper parts of the packing.

The following example may be given, but it should be emphasized that the given data ought not to be generalized too freely. Furnace No. 4 after heat 550 was ready to be shut down, but as the blast was being used on another furnace it could not be helped right away. However, as it was evident that it would have to be shut down unless something was done, it was determined to try the cure. The results are given in Table V.

The analyses of the waste gases, with badly shut doors, were as follows:

	Per cent. CO_2.	Per cent. O.	Per cent. CO.
Average before applying the blast.....	13.8	5.2	0.0
After applying the blast.....	10.2	8.0	0.0

Furnace No. 4 then worked without delays, in the improved method shown, with an average hourly output of 6 tons from December 17 to January 12. Not only was the life of the furnace increased by 25 days, but its hourly output before shutting down was raised by about 1½ tons. The changes brought about in the pressure conditions are shown in Figs. 5 to 8. It is seen that the partial vacuum in both the upper and lower parts of the air regenerators is changed to a positive pressure, by applying the blast. The amount of blast was so arranged that the pressure in the upper part was about equal to zero. As soon as the motor was stopped the former bad conditions prevailed as shown at X_1, X_2, X_3, X_4 and X_5 in Figs. 5 to 8. The tapping times are shown by A_1 A_2 A_3 A_4 and A_5, which indicate the changed time of the length of the heat.

TABLE V.—CHANGE IN OUTPUT BROUGHT ABOUT BY THE USE OF BLAST.

Date, 1911.	No. of heat in series.	Time of heat, hours.	Weight of heat, tons.	Hourly output Per heat, tons.	Aver. ton.	Remarks.
Dec. 12	544	5.50	28.8	5.23		
Dec. 12	545	6.25	32.6	5.21		
Dec. 12	546	5.75	27.5	4.78		
Dec. 13	547	5.75	27.4	4.76		
Dec. 13	548	5.50	28.5	5.19		
Dec. 13	549	7.75	35.2	4.55		Dead heat
Dec. 14	550	6.75	30.5	4.51		Dead heat
Dec. 14	551	6.00	31.8	5.03		
Dec. 14	552	7.25	30.2	4.17	4.66	
Dec. 15	553	7.25	30.0	4.14		Dead heat
Dec. 15	554	5.25	32.5	6.20		Dead heat
Dec. 15	555	6.25	28.5	4.56		Dead heat
Dec. 15	556	6.00	27.0	4.50		Dead heat
Dec. 16	557	8.25	35.4	4.30		Cold heat
Dec. 16	558	7.00	30.8	4.40		Cold heat
Dec. 16	559	8.25	31.0	3.77		Cold heat
Dec. 17	560	7.50	35.7	4.76		Cold heat
Dec. 17	561	4.25	31.2	7.03		Blast started
Dec. 17	562	5.25	35.4	6.75		
Dec. 17	563	5.50	35.6	6.49		
Dec. 18	564	5.75	31.0	5.40		12 hours
Dec. 18	565	5.00	34.0	6.80		Sunday rest
Dec. 19	566	5.25	28.3	5.39		
Dec. 19	567	5.00	34.2	6.85	6.03	
Dec. 19	568	4.75	26.8	5.62		
Dec. 19	569	5.75	32.5	5.81		
Dec. 20	570	7.00	35.0	5.00		
Dec. 20	571	5.25	30.0	5.72		
Dec. 20	572	5.00	30.8	6.15		
Dec. 20	573	5.25	31.5	6.00		

At Donez-Jurjewka, with six furnaces, almost every month one of them is ready for a general repair, and as the blast can almost always render good service at this time, it is used from two to three weeks in the

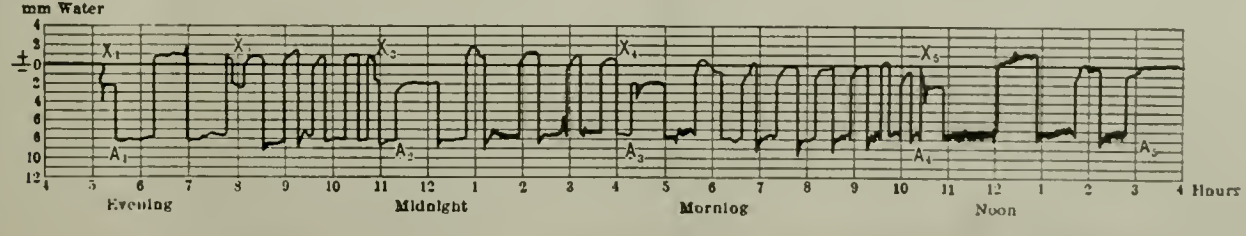


Fig. 8—Air Regenerator of an Old Furnace with Blast—Same Position as Fig. 6—Heats 574-8.

month and very considerably increases the output of the furnaces. It must be pointed out that even with the most careful use of the blast the furnace is strongly attacked, especially the front and back walls over the door arches. For this reason it is not recommended to use the blast before it is absolutely necessary.

Slagging and Filling Up of Regenerators.—The remainder of the paper takes up in detail the causes leading to the slagging and filling up of the regenerators. The author's conclusions are summed up in Table VI, which gives the calculated origin of the slag deposits in the slag pockets and checkers under his conditions, based on carefully made average analyses:

TABLE VI.—SLAG DEPOSITS IN REGENERATORS.

Materials from which the slag has been formed.	Percentage of these different materials In the gas regenerators.	In the air regenerators.
1. Additions, ore and limestone....	26.0	37.0
2. Furnace lining	0.8	1.5
3. Open hearth slag.....	28.2	16.0
4. Silica bricks	45.0	45.5

There is a big difference in the results from the air and gas regenerators. This is obviously due to the higher average temperature of the air chambers, their larger size, the greater space between the bricks of the checker work, and finally the difference in the pressure conditions which cause the gases to pass through the air chambers with greater velocity than through gas chambers. The main conclusion is that it is best to use only hard lump ore, instead of finely divided material.

With old furnaces it is often of great advantage to remove the topmost row or two of bricks. Of course, the furnace has to be cooled down and the greatest care must be exercised so as not to spoil the rest of the checker work.

All these practical helps, however, are only makeshifts toward the real protection of the regenerators. An excellent method is to build the slag pockets larger and across the whole width of the regenerators, as is being done in the more modern furnaces. One thing is certain, namely, that after the port question has been settled by the use of water cooling, changeable ports, or some other arrangement, the perfection and protection of the regenerators is the next one to be taken up.

THE WORLD'S CONSUMPTION OF NITRATE.

Some interesting statistics on the production and consumption of nitrate are given in a half-yearly report of W. Montgomery & Co. According to this there was an increased consumption of nitrate of soda in Europe of 147,000 tons for the first six months of 1912, which, added to the increase of 65,000 tons in the last six months, makes a total gain of 212,000 tons for the year. The figures for 1912 were 1,908,000 tons and for 1911, 1,696,000 tons. Consumption in the United States fell off 75,000 tons for the year, though other countries, including Egypt, show a steady increase. For the whole year of 1912 the world's consumption amounted to 2,504,000 tons, against 2,355,000 tons in 1911, or an increase of 6.3 per cent.

The consumption of nitrate in the various countries of Europe in 1911 and 1912, respectively, follows: Germany, 724,000 and 888,000 tons; Belgium, 294,000 and 295,000 tons; France, 332,000 and 349,000 tons; Netherlands, 145,000 and 174,000 tons; United Kingdom, 132,000 and 130,000 tons. Italian and Austrian ports show a decrease of 10.7 per cent, from 56,000 tons in 1911 to 50,000 tons in 1912. From 1893 to 1902 the total European increase in consumption amounted to only 226,000 tons, or a little over 28 per cent, while in the next 10 years the gain was 880,000 tons, or over 85 per cent.

The increase in the world's production and consumption from year to year since 1902 is shown herewith:

Year.	Production, Tons.	Consumption, Tons.
1902.....	1,351,000	1,259,000
1903	1,462,000	1,412,000
1904	1,535,000	1,447,000
1905	1,728,000	1,547,000
1906	1,795,000	1,636,000
1907	1,818,000	1,658,000
1908	1,940,000	1,732,000
1909	2,077,000	1,938,000
1910	2,427,000	2,241,000
1911	2,482,000	2,355,000
1912	2,540,000	2,504,000
Total	21,155,000	19,729,000

The difference of 1,426,000 tons between production and consumption represents losses in weight in shipping, losses at sea, stock in Europe and stock in Chile.

American consumption previous to 1893 seems to have remained almost stationary for several years around 100,000 tons, but in 1898 an improvement began to take place and since then progress has been fairly rapid. Farmers in the United States first became practically interested in the use of nitrate about the beginning of the present century. The increase of consumption in 1902 over 1892 amounted to 114 per cent, while the gain from 1902 to 1912 was 159.8 per cent. It is altogether probable that this increase will steadily continue, as there has been an increasing demand for the nitrate in every country where it has been introduced.

Production and consumption have been running a close race at times, especially during the past four years, and it is quite possible that the coming season will feel the effect of a limited supply. At present it seems that there is very little margin for expansion in consumption either in Europe or America.

The course of prices in the last six months of 1912 was in an upward direction until about the third week in October, when they slowly and reluctantly gave way. Refined quality has throughout had a difficult market because of a scarcity of sellers and the demands of the producers. During the past year or two some makers of this quality have ceased producing it.

METHODS OF ANALYSIS USED IN THE LABORATORIES OF THE ARMOUR INSTITUTE OF TECHNOLOGY.

Alloy Analysis by Volumetric Methods.

In case the alloy contains more than 5 per cent of copper, it is necessary to determine the tin and antimony from the combined oxides. Nickel also interferes but is not considered in this analysis. In either case, it is necessary to remove the oxides for the subsequent determination of the other metals.

Two .5 or 1.0 gram samples (depending on the amount of tin and antimony present) are weighed into casseroles, dissolved in 10 cc. concentrated nitric acid, digested some few minutes after solution has taken place, filtered undiluted through a gooch and washed with strong nitric acid. To the filtrates in Jena beakers 10 cc. of strong sulphuric acid are added and the solutions evaporated to fumes for lead.

The combined oxides and the asbestos mat are washed into a beaker with 15 cc. strong hydrochloric acid, digested till solution has taken place. The asbestos is filtered out through another gooch, washed with a minimum of dilute HCl and 10 cc. strong sulphuric acid added to the filtrate which is preferably in a 500 cc. Jena glass Erlenmeyer. Both solutions are evaporated to copious fumes. In case no interfering elements are present two .5 or 1.0 gm. samples of the original alloy may be dissolved in strong sulphuric with 4 to 5 gms. potassium sulphate and the process is the same as with the oxides alone.

While it is possible to titrate the tin following the antimony titration, yet much time is saved by using separate samples as the tin may be reduced while the antimony is titrated.

For antimony, the sulphuric acid solution is diluted with 50 cc. water and 10 cc. strong HCl added. A few grams of tartaric acid are placed in the solution and it is boiled vigorously for 1 to 2 minutes. It is then cooled and 25 cc. additional HCl and 110 cc. water added. It is then titrated with N/10 permanganate whose antimony value has been determined against mixtures of pure antimony and tin. The pink color fades rapidly but may be obtained accurate to the drop.

The other sample for the tin is diluted with 20 cc. water, 60 cc. strong HCl added and 40 cc. more water. In case the antimony in the sample is less than .15 gm., sufficient metallic antimony should be added to make up that amount. About .5 gram pure iron wire is added and the solution boiled while a rapid stream of CO_2 is passed through it continually. The boiling is continued for at least 20 minutes, or until the iron is dissolved. It is then cooled, with the CO_2 still passin gthrough it. When it has reached room temperature, a little starch solution and a lump of marble is placed in the flask and the solution titrated with N/10 iodine to the first permanent blue. The iodine solution should be standardized against mixtures of pure tin and antimony. The value obtained is close to the theoretical but not exact.

After the filtrates from the oxides have been taken to fumes with sulphuric acid, they are allowed to cool, diluted with about 100 cc. of water and 20 cc. alcohol, allowed to stand a few minutes and filtered through a Gooch, washing with 5 per cent H_2SO_4. The mat and precipitate are removed to a beaker, digested with 25 cc. strong hot ammonium acetate made by neutralizing ammonia with strong acetic acid. When digested sufficiently and the lead is all in solution, slight excess acetic acid is added and the solution diluted to 250 cc. with hot water. The lead is titrated with ammonium molybdate solution (4.5 grams per liter) using tannic acid as an external indicator. The first yellow color is the end point. The molybdate solution is standardized against pure lead sulphate and 1 cc. should equal about .005 grams.

One filtrate from the lead is boiled with about 1 cc. nitric acid, a few cc. bromine water added and the bromine color dispelled by boiling. It is then made alkaline with ammonia and acid with acetic acid. A slight excess of potassium iodide is added after the solution is cooled. The liberated iodine is titrated with N/10 thiosulphate, using starch as an indicator.

The second filtrate from the lead, or if duplicates are not required on the lead, the solution need not be filtered, is boiled with about a gram of metallic lead until the blue color has disappeared and the copper has all precipitated. If there is any doubt, a drop of the clear solution may be tested externally with potassium ferrocyanide and no color should result. The solution is cooled and allowed to settle, and is filtered as rapidly as possible, preferably through a Gooch. It is washed with cold water, keeping the copper covered as much as possible. The filtrate is made alkaline and boiled. Any precipitate of iron or aluminium hydroxide must be filtered off and may be ignited in platinum to the oxides. If the iron is to be determined, the oxides are fused with $KHSO_4$ and the melt dissolved in water and H_2SO_4. The iron is reduced with zinc and titrated with permanganate in the usual way.

The filtrate, or the whole solution is acidified with HCl until there is 3 per cent of strong acid by volume. The volume of the solution should be from 75 to 100 cc. for every .1 gram zinc. It is immediately titrated with potassium ferrocyanide solution which has been standardized against pure zinc oxide. The first precipitate is very flocculent but becomes less so towards the end point. Uranium acetate solution is used as an outside indicator and the first definite red-brown color on standing two minutes, is considered the end point.

RAPID DETERMINATION OF CARBON IN STEEL.*

By WILLIAM R. FLEMING.†

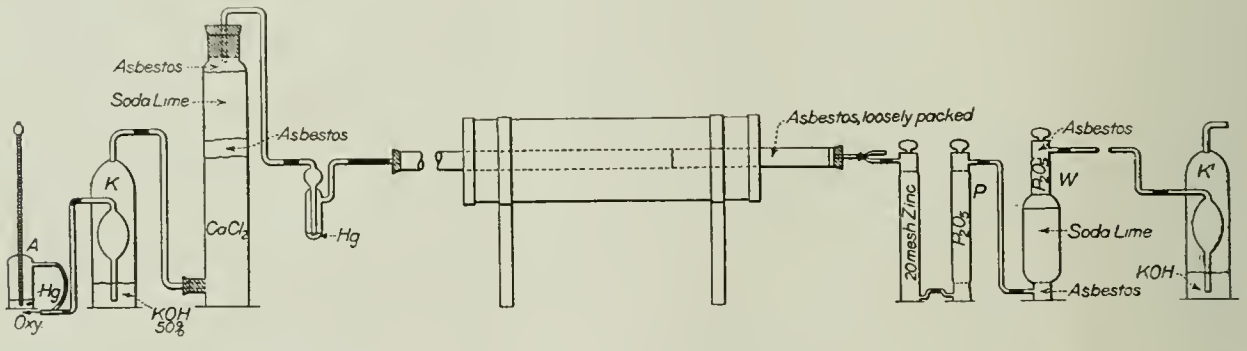
The method described here has been in daily use for about a year in the laboratory with which the writer is connected. The chemical principles involved are not new. The method differs only in manipulation from the ordinary direct combustion methods in general use. Since it represents a saving in time of more than 50 per cent as compared with the latter, and several chemists have asked the writer for a description, it has been thought worth while to publish it.

While the direct combustion method is far superior to the old solution method in ease of manipulation and in saving of time, it has its shortcomings. It is not absolutely reliable, for the sole reason that the steel does not always completely burn. Incomplete combustion is more liable to occur at any time, although, fortunately, with proper drillings, this seldom happens. The combustion is more liable to be incomplete if turnings from a lathe or thick chubby drillings from a diamond pointed drill are used. Curly drillings, not too thick, from a well sharpened twist drill, are by far the most reliable; in fact, the writer has never obtained low results due to incomplete combustion from this class of drillings.

Johnson, in his excellent little book, "Chemical Analysis of Special Steels, etc.," says that the combustion proper requires about 13 minutes. By "combustion proper" is meant the burning of the steel and transfer of carbon dioxide to the weighing apparatus. According to Johnson, 2 g. of steel require three minutes to burn, and the transfer of carbon dioxide to the weighing apparatus requires 10 minutes. So far as the writer is aware, the combustion proper is completed in not less than 12 minutes by any steel laboratory in this country.

In this laboratory the combustion proper never requires more than six minutes, in most cases only five. The results obtained are as accurate as those obtained by following the method as outlined in Blair, Johnson, or other books on steel analysis.

The Apparatus and Reagents.—The combustion train is shown in the accompanying figure, which is self-explanatory. Any of the ordinary trains, of course, can be used. The mercury pressure gauge A is necessary to follow properly the course of the combustion. The most important apparatus, however, is the absorption tube, W. While the form of apparatus shown may not be necessary, a *large diameter* tube containing soda lime must be used, and the soda lime must be protected by phosphoric anhydride. No other combination of reagents can be used to absorb the carbon dioxide in this rapid method. In fact, this form of apparatus and these reagents are the most efficient and reliable for the absorption of carbon dioxide in any method. It is infinitely superior to potash solution protected by potassium hydroxide or anything else.



Apparatus Employed in the Rapid Determination of Carbon in Steel.

On account of the violent combustion of the steel in this rapid method, as little sample as is consistent with good results is used. If the steel contains over 0.40 per cent of carbon, 1½ g. are used; if below 0.40 per cent, 2 g.

Before starting a determination the ground glass stopper in the top of P is closed, and the oxygen is turned on until the mercury in A shows a pressure of about 4 in. After connecting the weighing apparatus, the stopper in P and the bottom and top stoppers in the weighing apparatus are opened, in the order named. A rapid stream of oxygen sweeps the ordinary air from the glass tubing beyond the absorption tube. This glass tubing is ⅛ in. bore (at least 1 ft. long) and answers just as well as a guard tube con-

*Laboratory Andrews Steel Co., Newport, Ky.
†From the Iron Age.

taining calcium chloride or soda lime. The potash bottle at the end of the train is used only to satisfy one's curiosity to know whether the oxygen is flowing through the train. In fact, both potash bottles shown in the figure are absolutely unnecessary as absorbents of carbon dioxide, each being used to indicate the flow of gas.

Combustion Procedure.—Thin, curly drillings are spread out the entire length of a clay boat 3 in. long. The boat is quickly pushed into the combustion tube and the oxygen turned on rapidly until the mercury shows a pressure of several inches (which depends on the resistance of the train to the passage of the gas). A pressure of 4 in. in the train as made up in this laboratory usually gives a current of 400 cc. per minute. Twenty or 30 seconds after the boat is pushed into the furnace the column of mercury will begin to recede, which marks the beginning of combustion. The flow of oxygen is immediately increased so that it continues to leave the exit end of the train at the same rate it escaped before combustion began, namely, about 300 to 400 cc. per minute. In 30 seconds 1½ g. of steel will burn completely and 2 g. in 45 seconds. As a rule, the steel is completely burned one minute after being placed in the combustion tube. The end of combustion is noted by the rapid rise of the column of mercury. The flow of oxygen (400 cc. per minute) is continued for four more minutes. The two-way stop following the combustion tube is closed immediately after shutting the oxygen valve. Then close the top stopper in P and the bottom and top stoppers in W in the order named. Disconnect W, open the lower stopper to relieve the excess pressure, and weigh immediately. A duplicate apparatus is used as a tare, and is kept constantly at the side of the weighing apparatus, whether in the combustion or balance room. If proper care is taken, there is no necessity of ever waiting before weighing. After weighing, note the column of mercury in A. If it has receded, incomplete combustion may be suspected. A minute's observation will decide this point. While incomplete combustion never occurs with thin curly drillings, it is rather frequent with turnings or drillings from a diamond pointed drill, even though the latter were sieved through a 20-mesh screen.

The weighing apparatus is filled as shown in the figure. Baker's 12-mesh soda lime is used, the dust which passes an 80-mesh sieve being discarded. This, protected by phosphoric anhydride, makes the most efficient absorbent for carbon dioxide known. Oxygen containing carbon dioxide can be rushed through the apparatus used by the writer at the tremendous rate of 1,000 cc. per minute without it losing the slightest quantity of carbon dioxide or moisture. Coarse soda lime must not be used. Phosphoric anhydride is the only known drying agent that will trap all moisture swept from the soda lime when the oxygen is passing through the apparatus at the rate of 600 cc. per minute.

Accuracy with Rapid Flow of Oxygen.—The unusual feature of the method just described is the tremendous rate at which the oxygen is made to flow through the train. This is made possible only by the use of a specially constructed absorption apparatus containing soda lime protected by phosphoric anhydride. Most chemists are of the opinion that oxygen cannot be rushed through the apparatus as is done in this method and accurate results obtained. Johnson says that if the oxygen is rushed through the absorption apparatus during the combustion period low results are often obtained, due "probably" to carbon monoxide escaping from the hot part of the tube before it has had time to oxidize. Mr. Johnson must have assumed this to be the case, because he offered no proof that carbon monoxide actually did escape. Consistent daily results obtained by the method just described are ample proof that Johnson's statement is inaccurate. However, to disprove the statement directly the following experiment was carried out:

Ten combustions were run on a standard steel containing 1.025 per cent of carbon. In each combustion 1½ g. of steel was used and in every case the steel was burned in 30 seconds. The oxygen during the combustion period was leaving the train at the rate of 400 cc. per minute. After leaving the first absorption apparatus the gases were conducted through a second tube (porcelain ¼ in bore) filled with copper oxide and heated to 960 deg. in a second electric furnace. Immediately following this was placed a second weighing apparatus which was not disconnected to weigh until the entire 10 combustions had been run. The following table shows the results in detail:

TABLE I.

Time in combustion tube before combustion started.	Time required for complete burning of steel.	Total time of combustion proper.	Temp. of furnace.	Gain in weight of second weighing apparatus.	Per cent of carbon found.
45 sec.	60 sec.	6 min.	950 deg.		1.025
45 sec.	45 sec.	6 min.	950 deg.		1.023
30 sec.	45 sec.	6 min.	970 deg.		1.025
30 sec.	30 sec.	5 min.	970 deg.		1.018
30 sec.	30 sec.	5 min.	970 deg.		1.028
30 sec.	30 sec.	6 min.	970 deg.		1.027
30 sec.	30 sec.	5 min.	970 deg.		1.025
30 sec.	30 sec.	5 min.	970 deg.		1.025
30 sec.	30 sec.	5 min.	970 deg.		1.020
30 sec.	30 sec.	5 min.	970 deg.	0.0010 g.*	1.034

The above table not only shows that there is no possibility of carbon monoxide escaping unburned, but that excellent duplicate analyses can be obtained by this extremely rapid method. The minute gain in weight of the second weighing apparatus was not due to absorption of carbon dioxide. This was demonstrated by running a second set of ten combustions in which a phosphoric anhydride tube was placed between the second combustion tube and the second weighing apparatus. In this case the second weigh-

*Entire gain for ten combustions.

ing apparatus gained nothing, showing that oxygen can be rushed through the absorption apparatus during the combustion period at the enormous rate of 400 cc. per minute and not the slightest trace of carbon monoxide escape monoxidized.

Since the burning steel spatters more than in the ordinary method a platinum cylinder should be used to protect the combustion tube. Otherwise the tube should be taken out of the furnace frequently and the clinging oxide removed by tapping lightly with a stiff steel rod.

A word of caution must be added concerning the use of clay combustion boats. Many clays are unfit for use because during combustion of the steel they give up carbon dioxide which is not liberated by preparatory heating. Such clays can be burned for several hours at 1,000 deg. in an atmosphere of oxygen; yet when used for a combustion they give high results —in some cases extremely high. This is, perhaps, due to the violent heat generated during combustion and to the slagging of the steel with the boat, thus liberating carbon dioxide which was not expelled by preliminary heating. A good clay, free from difficultly decomposed carbonates, mixed with an equal part of alundum, makes the most satisfactory boats. If a good clay can be found, the clay boat is by far the best and the most economical to use. No sand, alundum, or anything else need be used to protect the boats in this rapid method, because they do not protect. A new boat is used for each combustion.

BRITISH STANDARD SPECIFICATIONS FOR SOAP LYE AND SAPONIFICATION CRUDE GLYCERINES.

The following specifications for soap lye and saponification crude glycerines were approved at a general meeting of crude glycerine makers, buyers, and brokers, held in the Whitehall rooms, London, on Oct. 3 last.

SOAP LYES CRUDE GLYCERINE.

Analysis to be made in accordance with the International Standard Methods, 1911.

Glycerol.—The standard shall be 80 per cent glycerol. Any crude glycerine tendered which tests 81 per cent, glycerol or over shall be paid for at a *pro rata* increase, calculated as from the standard of 80 per cent. Any crude glycerine which tests under 80 per cent glycerol, but which is 78 per cent, or over, shall be subject to a reduction of 1½ times the shortage, calculated at *pro rata* price, as from 80 per cent. If the test falls below 78 per cent, the buyer shall have the right of rejection.

Ash.—The standard shall be 10 per cent. In the event of the percentage of ash exceeding 10 per cent, but not exceeding 10.5 per cent, a percentage deduction shall be made for the excess calculated as from 10 per cent, at *pro rata* price, and if the percentage of ash exceeds 10.5 per cent, but does not exceed 11 per cent, an adidtional percentage deduction shall be made equal to double the amount in excess of 10.5 per cent. If the amount of ash exceeds 11 per cent, the buyer shall have the right to reject the parcel.

Organic Residue.—The standard shall be 3 per cent. A percentage deduction shall be made of three times the amount in excess of the standard of 3 per cent, calculated at *pro rata* price. The buyer shall have the right to reject any parcel which tests over 3.75 per cent.

SAPONIFICATION CRUDE GLYCERINE.

Analysis to be made in accordance with the International Standard Methods, 1911.

Glycerol.—The standard shall be 88 per cent. Any crude glycerine tendered which tests 89 per cent or over shall be paid for at a *pro rata* increase, calculated as from the standard of 88 per cent. Any crude glycerine which tests under 88 per cent, but is 86 per cent, or over, shall be subject to a reduction of 1½ times the shortage, calculated at *pro rata* price as from 88 per cent. If the test falls below 86 per cent the buyer shall have the right of rejection.

Ash.—The standard shall be 0.5 per cent. In the event of the percentage of ash exceeding 0.5 per cent, but not exceeding 2 per cent, a percentage deduction shall be made equal to double the amount in excess of 0.5 per cent. If the amount of ash exceeds 2 per cent, the buyer shall have the right to reject the parcel.

Organic Residue.—The standard shall be 1 per cent. A percentage deduction shall be made of twice the amount in excess of the standard of 1 per cent, calculated at *pro rata* price. The buyer shall have the right to reject any parcel which tests over 2 per cent.

The British Executive Committee recommends that the following form of analytical report should be adopted:

	Percentage.
Total Acetyl Value as Glycerol.	
*Acetyl Value of Residue as Glycerol.	
Less Allowance.	
Correction for Acetyl Value of Residue as Glycerol.	
GLYCEROL (I.S.M. 1911)	
Ash.	
Organic Residue.	
Free Acid in terms of Na_2O.	
Alkali, Hydroxide, and Carbonate, in terms of Na_2O.	

*Not determined if Total Organic Residue is 2.5 per cent or under in the case of Soap Lye Crude, and 1.0 per cent in the case of Saponification Crude Glycerine.

In Mr. William Tattersall's cotton-trade circular for 1912 an analysis of the stock-taking results of 26 cotton-spinning companies at the end of December shows a profit on share capital of nearly 11 per cent per annum, while on share and loan capital combined the profit is nearly 8 per cent per annum, after allowing interest on loans. With regard to the future course of trade, Mr. Tattersall says that weavers of cloth have now had about two and a half years' profitable experience, but there are no signs of any falling off in demand, and most manufacturers are assured of full work up to the middle of 1913. In the spinning section the current year should be even better than the past 12 months.

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HARRY McCORMACK, Editor.

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A New Copper Alloy.

Metallurgists all over the country have been very much interested recently in the production of non-corrosive alloys of the various metals. Such alloys are of particular interest to men engaged in chemistry and chemical engineering. The following account of a new copper alloy as given by Robert Grimshaw in a recent issue of the Metal Industry will probably be of value.

In researches made as to the influence of the addition of cobalt to the more important metals, it was found that an alloy of cobalt and tin of about 40 and 60 was especially resistant to acids, even to the most concentrated nitric acid and such as is mingled with chlorides, as for instance common salt, which renders it more corrosive; partaking of aqua regia.

As this alloy is exceptionally brittle, hence almost useless where it is necessary to work it, this discovery was almost worthless from the practical standpoint. It was further found, however, that this alloy, dissolved in other metals which better permit mechanical working—as for instance copper—gave them a greater chemical-resistance. When, for instance, enough of the above mentioned cobalt-tin alloy is dissolved in copper to make alloys containing from 80 to 95 per cent of copper and 20 to 5 per cent of the cobalt and tin, there is obtained a series of alloys which may not only be well filed, bored, turned, forged, etc., but have also a high degree of chemical resistance.

The alloys lying in these series were so little attacked by dilute acids (especially nitric) that the time theoretically required to corrode away a layer of 1 mm. (0.0394 inch) thick was calculated to be five to seven years, even on the assumption that the corrosion would take place at an even rate throughout the entire time. In reality, however, the rate of corrosion diminished, which is readily explained by the fact that where chemical action takes place the more lightly attacked element is removed, while the less soluble remains on the surface and acts as a protective coating.

The preparation of these alloys can take place in the usual manner, but it seems to have been found by the experiments above named that it is best to make the cobalt-tin alloy first and dissolve it in the copper.

Meeting of the American Chemical Society.

The American Chemical Society will hold its first meeting under the new arrangement for meetings at Milwaukee from March 25 to 28 inclusive. The custom of this society has been to hold their semi-annual meetings one in the latter part of December, the other in the latter part of June of each year. The winter meeting has always been held in connection with the American Association for the Advancement of Science. Both of these organizations grew until it was rather difficult to secure a meeting place for all of the sections of the larger organization unless the meeting place selected was one of the largest cities in the country. This together with the fact that many of the scientists of the country were objecting to spending the greater part of their holiday vacation attending these meetings has lead to the change in the policy of the American Chemical Society. The meetings of this society will now be held in the spring and in the autumn, the Milwaukee meeting being the first one under the new arrangement.

There are many industries of interest to chemists located in and around Milwaukee. Among other places of interest to be visited is the State University of Wisconsin, one day being taken from the meeting to visit Madison, Wisconsin, to look over the university located there and also visit the First Products Laboratory located at that point. The particular lines of manufacture in Milwaukee in which the chemist will be interested are those connected with the tanning industry, the manufacture of iron and steel, by-product coke and gas, the manufacture of glue, the manufacture of refrigerating machinery, and the manufacture of automobiles and automobile parts. There are also large flour milling interests located here.

The usual provision is made for the social entertainment of the visitors. The customary number of sections have meetings provided for.

Crude Oil as Fuel.

There has been a recent marked advance in the price of crude petroleum products which have been in use as fuel in many industries. Particularly in some of the iron and steel industries has it been used as fuel in tempering and reheating furnaces. The past twelve months has marked an advance of almost 100 per cent in the price of oils from certain districts. This advance has been most marked on oils from the Pennsylvania district and others of similar character in which the yield of light distillates is high. About the same percentage advance is noted in all oils, but the price per barrel being highest for those noted. The following table from a recent issue of the Oil Paint & Drug Reporter shows how marked this advance has been:

PRICES PER BARREL AT WELLS.

	Prevailing basis.	Last week's.	Last year's.
Pennsylvania	$2.40	$2.05	$1.50
Cabell	2.00	1.65	1.12
Mercer, black	1.93	1.58	1.05
New Castle	1.93	1.58	1.02
Corning	1.93	1.58	.95
North Lima, Ohio	1.31	1.28	.92
Indiana	1.26	1.23	.87
Princeton, Ind	1.14	1.08	.75
Somerset, Ky	1.32	1.20	.83
Ragland, Ky	.70	.68	.48
Illinois, light	1.14	1.11	.75
Illinois, heavy	1.14	1.11	.65
Kansas and Oklahoma	.88	.83	.57
Corsicana, Tex., light	.95	.90	.60
Corsicana, heavy	.70	.70	.50
Henrietta, Tex	.95	.90	.60
Electra, Tex	.95	.90	.60
Caddo, La., light	.91	.91	.69
Caddo, heavy	.60	.60	.41

German Sugar Production and Exports.

The U. S. Consul at Madgeburg, reports that the German sugar production in the first quarter of the current campaign (Sept. 1 to Nov. 30, 1912) was the largest in 10 years; 36,736,700 hundredweight of sugar was produced in this period from a total of 242,486,300 hundredweight of beets (the German hundredweight equals 110.23 lbs.). In the corresponding quarter of 1910, 245,975,200 hundredweight of beets were used by the factories, but the sugar output was not so great as in 1912. Exports also were unusually heavy.

The following table gives the production and export figures of the November quarters of the years 1903-1912, inclusive, in German hundredweight:

November quarter.	Sugar beets used. Cwt.	Sugar produced. Cwt.	Sugar exported. Cwt.
1903	206,914,700	26,034,000	4,123,800
1904	181,524,500	24,706,500	3,568,600
1905	221,063,000	30,051,000	3,669,900
1906	219,365,000	30,262,100	6,978,500
1907	206,560,500	28,937,800	4,347,100
1908	210,026,900	32,898,400	3,341,400
1909	218,331,000	30,477,200	4,027,800
1910	245,975,200	36,534,300	3,671,700
1911	163,695,800	23,682,900	1,538,200
1912	242,486,300	36,736,000	5,310,600

Such large shipments in the first quarter have already brought decided relief to the sugar industry. England is naturally the chief buyer, but American purchases have also been of importance.

India's Trade in Drugs and Chemicals.

During the official year ended March 31, 1912, Bombay imported chemicals, drugs, and medicines to the value of $923,039, against $870,361 in the previous fiscal year. These imports came almost wholly from Europe, 69 per cent of the trade being supplied by the United Kingdom, and the larger part of the balance divided between Germany, Italy, and Belgium. Imports from the United States are so small that they are included under the general heading of "Other foreign countries."

The chief articles purchased were: Alum, 31,554 hundredweight, valued at $39,019; arsenic, 698 hundredweight, worth $7,253; bleaching materials, 5,938 hundredweight, value $20,473; borax, 2,397 hundredweight, value $11,913; and calcium carbide, 1,155 hundredweight, value $6,501. Other imports consisted of 11,820 hundredweight of copperas; disinfectants valued at $36,411; soda compounds, caustic soda, and sodium carbonate worth $147,128; sal ammoniac, $46,016; sulphur, $16,166; sulphuric acid, $73,318; and chemicals not elsewhere specified $496,932. This last group included a number of individual articles of which the most important were camphor, quinine and alkaloids thereof, and patent and proprietary medicines. Quinine purchases amounted to $71,800, of which about 10 per cent in different preparations came from the United States.

Dr. Alsberg, the New Chief of the Bureau of Chemistry.

Dr. Carl L. Alsberg, chemical biologist of the Bureau of Plant Industry, U. S. Department of Agriculture, who has been appointed chief of the Bureau of Chemistry by President Taft to succeed Dr. Harvey W. Wiley, was born in New York City and is a graduate of Columbia University. He studied abroad at a number of the leading universities, including the University of Berlin, where he did considerable work under Professor Schmiedeburg, the eminent Pharmacologist. Upon his return from Germany he became head of the Department of Biological Chemistry of the Harvard Medical School, and from that post entered the Government service. He is a member and ex-Secretary of the Council of Boston Society of Medical Sciences, councillor of the American Chemical Society, chairman of a section of Biological Chemistry of the American Chemical Society, associate editor of *Chemical Abstracts*, collaborator of the *Journal of Pharmacology and Experimental Therapeutics*, and is the author of a long list of scientific papers in both German and English.

In an interview in the *Public Ledger* of Dec. 22, 1912, Dr. Alsberg, while very modest and conserva-

tive, yet gives the assurance of recognizing the responsibilties of his position not only to the public but to the manufacturer. He says:

I believe that most manufacturers and handlers of foodstuffs want to do the right thing, but most of them don't know exactly what is the right thing. The whole subject of food inspection and the demand for pure foods is new. When the Bureau of Chemistry was established there were no standards, no guides of any sort. Everything had to be worked out, and it's been slow work. Only a few things definitely have been determined for this analysis of foods. To establish standards is not the work of days, but of years. When we arrive at what is the standard then we must show the manufacturer how to bring his products up to the standard.

If we tell a man who is putting up dried fruit that he must not use certain preservatives to prevent the development of insect life in the product, we have gone only half way if we do not show him how he can take care of his fruit in such way as to dispense with the forbidden preservative and still insure the keeping qualities of the product.

Essential and Edible Oils.

The following extract regarding the work of the laboratories of the U. S. Department of Agriculture is taken from the report for 1912 by the chemist of that department:

Citrus By-Products.—The field work of this laboratory has made splendid progress during the year. The experimental plant has been installed at Los Angeles, Cal., for making practical commercial tests upon the production of citrus by-products early in the coming winter. Experiments have been tried both in the field and at the laboratory in Washington, and many practical experiments now await only the practical field test as a final proof of their efficiency. The chief of the laboratory has visited several commercial plants and made practical tests as to the availability of the manufacturers' machines for use in this work, and no little benefit has been derived from the experience gained.

Essential Oils Used for Flavoring Food Products.—Much time has been devoted to research work on the methods for the determination of the active constituents of essential oils and to general methods for the detection of their adulteration. It was found that many of the methods of analysis, as well as physical constants, given in the current edition of the *Pharmacopoeia* were not up to date, so that the work on each individual class of oil has had to be done simultaneously with a special investigation upon samples of known origin. It is hoped that the results of these investigations will shortly be published as a circular.

LETTERS TO THE EDITOR.

Sea-weed, Potash and Iodine.

It has given me great pleasure to read the article of Mr. Frank K. Cameron in the September issue of "The Journal of Industrial and Engineering Chemistry," page 690, entitled "Sea-weed, Potash and Iodine." Naturally, I will overlook such expression in his reply as "captious," "misleading and quite mischievous statements" for the simple reason, that even if my critique of his "preliminary reports" has struck him unfavorably, I can assure him, that to do so was the least of my intentions.

The question is of such vital importance for this country, that the interested part of the public, especially the farmers demand a lucid explanation of the following:

(1) Can the United States partly or wholly satisfy its great demand for potash by the Pacific coast sea-weed?

(2) Can the potash obtained from sea-weed be placed on the market at a price enabling it to compete with the German potash?

My answers to these questions have been and will continue to be:

(1) That in comparison with the enormous demand in this country a relatively small amount of potash can be obtained in this way.

(2) That the success of a potash-industry and also the market price of potash manufactured from sea-weed is dependent upon the obtainable biproducts, especially iodine.

Mr. Cameron *has not as yet* made a single objection to these statements, nor has he with a word even touched the second important factor in this discussion, except that he has incidentally mentioned, that it would be of little importance whether the iodine in the sea-weed were used or not.

In the year 1910 hence, previous to our well-known potash dispute with Germany, I presented to the Department of Commerce and Labor (Bureau of Fisheries) a proposition for utilization of the Pacific coast sea-weed.*

In reference to this article, Mr. Cameron writes, that I have represented in that process the iodine as the main product and the potash as a side issue. In his opinion the nomenclature should have been reversed. In such a matter a person can suit himself, and as far as I am concerned it does not make a particle of difference which is to receive either appellation. In the fact, that the sea-weed contains these two substances lies its chief technical value. Moreover, on this technical value alone can an eventually successful sea-weed industry be based. The mentioned technical data are to be found in Senate document No. 190, Sixty-second Congress, second session, "Analyses of the Pacific Kelp, by T. W. Turrentine."

Inasmuch as these analyses give results whose correctness I have no right to doubt, my acquaintance with the Pacific coast sea-weed can be taken for granted, without necessitating my personal appearance on the field. And yet I might mention, that already ten years ago, through the courtesy of the Norwegian Consul in Tacoma, I had the opportunity of making preliminary examinations of the identical species, and

*Incidentally I might mention that I have never laid the matter before Mr. Cameron, who nevertheless has probably read it and profited thereby.

I am sorry to say, that I found a different and a more favorable percentage of iodine in these marine plants on the west coast, than that reported by Mr. Turrentine.

Upon the preliminary investigations as a basis, Mr. Cameron states, that the country's yearly demand of 1,250,000 tons of potash now imported—and even more than that—could easily be supplied from this domestic source. In answer to this, we have only to quote from Mr. Turrentine's report in the above mentioned Senate Document, page 261. "The extraction of iodine (and potash) is among the newer of the kelp industries of Japan. * * * That the industry there has probably reached its greatest possible development is indicated by the fact, that the manufacturers are already experiencing considerable difficulty in obtaining sufficient raw material wherewith to operate." The estimated output of iodine in Japan is about 250,000 kin (336,000 lbs.) a year, which corresponds to an annual production of about 100,000 tons of potash salts, and yet it is a well-known fact, that the extensive coasts of the Island Empire possess a remarkably rich vegetation of sea-weed. The conclusions we can draw from the above facts are self-evident.

Mr. Cameron furthermore does not trust me to calculate the cost of obtaining the raw material nor the cost of manufacturing the products and writes: "Mr. Knudsen's estimates are absurdly wide of the mark." Yet a person might think that with my twenty years' experience in this line, I would be better fitted to estimate cost than Mr. Cameron, who "cannot give any figures with a claim for accuracy for there is not sufficient existing experience on which to base accurate calculations." His opinion is, that the raw material—the dried sea-weed or the ash of the same—can be obtained cheaper on the Pacific coast than in Norway,* Scotland or Japan, a statement which needs proofs.

In the above mentioned countries a sea-weed industry is carried on, using a species, which, according to Mr. Turrentine's analyses, contains less potash than the Pacific Kelp, but more of the higher priced iodine. In Norway, for example, the raw material comes from the species Laminaria digitata, commonly known as "drift-kelp." In the spring—after the natural budding of this marine plant—stormy weather brings up enormous quantities of the sea-weed, leaving it for miles and miles in a deposit on the shore, 20-30 ft. wide and 5-6 ft. deep.

From the beach it is carried by carts or on tracks to the farms, where it is dried and burned. I have personally visited farms where as many as 500 carts and thousands of persons were kept busy. The cost of labor is $1 a day per man and $2 for a man and horse. The contents of this sea-weed ash are 26-35 per cent of actual potash (K_2O) and 0.7-1.2 per cent of iodine.* The Scotch and Norwegian manufacturers buy up this kelp ash at the farm for $22 a ton, this eliminating middle men. With this price of raw material and the present value of iodine, potash from this source can be put in the market against the German product, and the industry can moreover be carried on with some profit, which after all is the deciding factor in this sea-weed discussion.

Mr. Cameron is also of the opinion that "with large scale mechanical devices, the cost of harvesting and drying the kelp should not be one-tenth of what Mr. Knudsen estimates," while he himself admits that the mechanical apparatus for cutting stationary sea-weed have heretofore shown themselves unpracticable. The cut stationary sea-weed in spite of its somewhat greater percentage of valuable contents is bound to prove more uneconomical than drift kelp, and that has been my reason for demanding that more attention be paid the latter species—the "Torra."

To be sure potash does exist in this country, for example in feldspar. The question is how this potash can be obtained as a fertilizer or in other words how the potash in these rocks can be procured at a price reasonably like the existing market prices? So far it has been apparent that economic and not technical hindrances have prevented a commercial output from this source.

My calculations for the last of the production of kelp ash, potash and iodine, must be taken for their true value until Mr. Cameron, himself, has gained sufficient experience to pass judgment upon them.

It should make little difference whether I gained my experience in this country or not as only chemico-technical processes are needed and these have nothing to do with nationality. I am thoroughly acquainted with the different methods in use to recover the at present time known valuable substances in sea-weed, and I also know very well the most methods suggested to obtain new substances from these marine plants, some of which probably have not come to Mr. Cameron's attention yet, as "Norgin" and artificial rubber.

For the present Mr. Cameron's calculations may remain at their intrinsic value and for his own use. In passing, I am in a position to state that the most uneconomic way of utilizing the sea-weed is as a direct fertilizer and as such it has been used for centuries. "Pulverized sea-weed" has been known for years, but even that has been accepted as a definitely settled question.

Outside of my previous remarks on the calculations of Mr. Cameron, I will not refer to them any more for they are so improbable, that no manufacturer of potash and iodine from sea-weed would be apt to accept them to base an industry upon them.

Philadelphia. HENRIK KNUDSEN.

*Mr. Cameron also includes Sweden and Denmark as kelp producing countries, but these countries do not produce kelp at all.

*In accordance with Mr. Turrentine's analyses the ash of certain Laminaria of the Pacific coast kelps contains from 15 to 46 per cent actual potash and from 0 to 0.9 per cent of iodine.

RECENT PATENTS.

The following patents relating to industrial and engineering chemistry are reported by C. L. Parker, solicitor of chemical patents, McGill Building, Washington, D. C.

1,045,889. Process of Making *Sodium Bicarbonate* and Organic Substances from Soda-Pulp-Waste Liquor. Erik Ludvig Rinman, Harnas, Sweden. Patented Dec. 3, 1912.

1,045,895. *Cellulose—Ester Solution.* Otto Schmidt, Mannheim, Georg Lutz, Ludwigshefen-on-the-Rhine, and Theodor Eichler, Mannheim, Germany, assignors to Badische Anilin & Soda Fabrik, Ludwigshafen-on-the-Rhine, Germany. Pat. Dec. 3, 1912.

1,046,043. Method and Apparatus for *Reducing Chemical Compounds.* Ezechiel Weintraub, Lynn, Mass., assignor to General Electric Company, a corporation of New York. Pat. Dec. 3, 1912.

1,046,160. Manufacture of *Ethyl Alcohol* by Fermenting Sulfite Liquor. Per Gosta Ekstrom, Harnas, Sweden, assignor to Aktiebolaget Ethyl, Faulun, Sweden. Pat. Dec. 3, 1912.

This is an improvement in fermenting sulfite liquor for the purpose of manufacturing ethyl alcohol therefrom by the addition of urine to the liquor to be fermented.

1,046,232. Manufacture of *Vanadium Cast-Iron.* Frederick W. Sickle, Newington, Conn. Pat. Dec. 3, 1912.

1,046,475. Process of Making *Paper* and Products Thereof. Robert A. Marr, Blacksburg, Va. Pat. Dec. 10, 1912.

1,046,538. Treatment of *Flax-Straw.* Harry Preston Bassett, Newark, Delaware. Pat. Dec. 10, 1912.

1,046,594. Treating Mother-Liquors Formed in Making *Alkali Perborates.* Fritz Hoyler, Arthur L. Gardner and Hans Foersterling, Perth Amboy, N. J., assignors to The Roessler & Hasslacher Chemical Co., New York, N. Y. Pat. Dec. 10, 1912.

1,047,082. Process of Manufacturing *Beet Sugar.* Vaclav Kolarik, Owosso, Michigan. Pat. Dec. 10, 1912.

1,047,132. Process of Treating the *Residual Caustic Liquor* Resulting from Digestion of Wood. James M. Neil, Toronto, Ontario, Canada. Pat. Dec. 10, 1912.

1,047,174. Method of Briqueting *Flue-Dust.* George L. Collard, Sharon, Pa. Pat. Dec. 17, 1912.

1,047,198. *Artificial Fuel* and Process of Making the Same. Blake E. Gamble, Bowmansdale, Pa. Pat. Dec. 17, 1912.

1,047,236. Method of *Regenerating Contact Mass.* Weston M. Kelsey, Depue, Ill., assignor to New Jersey Zinc Co., New York, N. Y., a corporation of New Jersey. Pat. Dec. 17, 1912.

1,047,360. Process of Separating *Zinc and Lead* from Mixed Sulfids. Carl August Louis Wilhelm Witter, Hamburg, Germany. Pat. Dec. 17, 1912.

1,047,440. Process of Producing *Calcium Phosphamid.* Samuel Peacock, Chicago, Ill., assignor to The Southern Electro-Chemical Co., New York, N. Y., a corporation of New Jersey. Pat. Dec. 17, 1912.

1,047,481. *Concrete Binder* and Preservative. Nelson B. Arnold, New York, N. Y. Pat. Dec. 17, 1912.

1,047,502. Method of Treating *Fruit.* Elsie L. P. Thomas, Philadelphia, Pa. Pat. Dec. 17, 1912.

1,047,576. Solid Compound of *Nitric and Sulfuric Anhydrids* and Process of Making Same. William Schultze, New York, N. Y., assignor to General Chemical Company, New York, N. Y., a corporation of New York. Pat. Dec. 17, 1912.

This is a solid composition containing sulfuric and nitric anhydrids and water in quantity less than that corresponding to three molecular proportions of the compound, which has the following properties, viz.: that said compounds at ordinary temperatures form a water clear, white or yellowish, hygroscopic crystalline mass, sometimes displaying well-defined rectangular plates, which has a specific gravity of about 2.18, melts at 93-104° C., and on further heating decomposes with evolution of nitrous fumes.

1,047,654. Process of Manufacturing *Oxygenerated Salts.* George Francois Jaubert, Paris, France. Pat. Dec. 17, 1912.

1,047,864. Process of Producing *Phosphorus* from Mineral Phosphates. Frank S. Washburn, Nashville, Tenn. Pat. Dec. 17, 1912.

1,047,968. *Tanning* Compound. John H. McWirter, Grand Valley, Okla. Pat. Dec. 24, 1912.

The compound includes a mixture of extract of alfalfa and gum gambier.

1,048,138. Method of *Vulcanizing* Vulcanizable Articles. William W. Duncan, Boston, and Nelson E. Tousley, Watertown, Mass., assignors to Hood Rubber Co., a corporation of Massachusetts. Pat. Dec. 24, 1912.

1,048,161. *Suspensible Sulfur* and Process for Producing Same. Homer W. Hillyer, Farmington, Conn., assignor to Thomsen Chemical Co. Pat. Dec. 24, 1912.

1,048,207. *Priming Mixture.* Henry C. Pritham, Bridgeport, Conn., assignor to The Union Metallic Cartridge Co., Bridgeport, Conn., a corporation of Connecticut. Pat. Dec. 24, 1912.

1,048,231. Method of Manufacturing *Carborundum Filaments.* Frank C. Thomas, Pittsburgh, Pa., assignor to The Nernst Lamp Co., a corporation of Pennsylvania. Pat. Dec. 24, 1912.

1,048,247. *Recovery of Sulfuric Acid and Iron* from Ferrous-Sulfate Sludge. Charles A. Weeks, Philadelphia, Pa. Pat. Dec. 24, 1912.

1,048,541. Process for the Treatment of *Ores.* Joseph Irving, Salt Lake City, Utah. Pat. Dec. 31, 1912.

1,048,578. Safety-Powder for *Blasting*. Gershom M. Peters, Cincinnati, Ohio. Pat. Dec. 31, 1912.

1,048,695. Composition for *Waterproofing Concrete*. Aaron C. Horn, New York, N. Y. Pat. Dec. 31, 1912.

1,048,699. Process of Manufacturing *Urea*. Heinrich Immendorff and Hubert Kappen, Jena, Germany. Pat. Dec. 31, 1912.

1,048,815. Solid *Disinfecting Composition* Containing Oil. Carleton Ellis, Montclair, N. J., assignor to Ellis-Foster Company, a corporation of New Jersey. Pat. Dec. 31, 1912.

1,049,054. Process for *Removing Scale*. Frank E. Coombs, Au Sable Forks, New York. Pat. Dec. 31, 1912.

1,049,141. Process of *Desiccating Milk*. Emil Passburg, Berlin, Germany. Pat. Dec. 31, 1912.

1,049,193. Process of Obtaining Pure *Tungstic Acid*. Tokusei Ban, Tokyo, Japan. Pat. Dec. 31, 1912.

1,049,201. Process for *Recovering Copper* from the Wash Liquors Employed in the Cuprammonia-Cellulose Process. Emile Bronnert, Niedermorschweiler, Germany, assignor to Verinigte Glanzstoff-Fabriken A. G. Elberfeld, Germany. Pat. Dec. 31, 1912.

1,049,251. Composition of Matter to be Used as *Coating*, Size, or Paste. Maxmilian Mayer and Joseph N. Wiggin, Orange, and Robert W. Cornelison, Bloomfield, N. J., assignors to H. B. Wiggin's Sons Company, a corporation of New Jersey. Pat. Dec. 31, 1912.

The composition consists of about 150 pounds of granular plaster of Paris, 60 lbs. of Paris white, 21 lbs. of finely comminuted glue, 55 lbs. of flour, and 2½ lbs. of glycerine.

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PURIFYING WATER BY SEDIMENTATION AND FILTRATION.

By EDWARD K. HAMMOND.

The problem of purifying water to render it fit for drinking purposes is necessarily one which differs considerably, according to the character of the available supply. The method of purification by sedimentation and filtration finds application where the raw water carries a considerable quantity of impurities, both in solution and suspension; a large percentage of the bacteria in the water are also removed by this treatment, so that it is only necessary to resort to some method of sterilizing to destroy the comparatively small number that pass through both the settling basin and the filters.

The method of purification of water by sedimentation and filtration is used on a large scale in the plant of the Hackensack Water Co., New Milford, N. J. This plant draws its supply from the Hackensack River and provides water for about 400,000 consumers. The territory supplied includes the city of Hoboken, N. J., and a number of suburbs on the Erie and Lackawanna Railroads, the supply pipes extending as far as Jersey City.

The first step in the process of purification used by this company consists of subjecting the raw water to the sedimentation treatment. For this purpose, a settling basin is used into which the water is pumped by Allis-Chalmers centrifugal pumps. There are two pumps provided for this purpose, each of which has a rated capacity of 32,000,000 gals. per 24 hours. These pumps are used alternately for periods of about eight days, one pump being kept in reserve so that it can take up the load if the other fails. After being in service for eight days, these pumps have to be shut down for a complete overhauling.

THE SETTLING BASIN.

The bottom of the settling basin is at a level of 2 ft. below datum and the centrifugal pumps are operated to maintain the water at a level of about 15 ft. above datum. The interior of the basin is lined with concrete and is open to the air. The basin is rectangular in shape and the water is fed in through a pipe at a level of 8 ft. above datum. This pipe extends in a semicircle around one end of the basin and has a series of man-holes on its upper side, through which the water is discharged.

The removal of impurities from the water that takes place in this basin is due to treatment by a method known as the "alum-process." As a matter of fact, however, the chemical used is not alum but commercial aluminum sulphate. This aluminum sulphate is added in the form of a water solution that is mixed in two tanks, each of which has a capacity of 300 gals.; these tanks are located on the third floor of the filtration plant. Beneath these tanks, on the second floor of the building, there are two storage tanks, each of which has a capacity of 1,000 gals. The storage tanks are connected with the two mixing tanks by a double system of pipes and valves, so that the contents of either mixing tank may be run into either of the storage tanks. The storage tanks, in turn, are connected with a second pair of small tanks, located on the same floor with them; the flow of the solution from the storage tanks into these small tanks is controlled by float valves. Pipes leading from this pair of small tanks carry the solution out to the settling basin, where it is discharged in the vicinity in which the raw water issues from the pipe that conveys it to the basin. The water is greatly agitated in this section of the basin, with the result that a thorough admixture of the water and aluminum sulphate solution is secured.

The chemist in charge of the plant varies the strength of the aluminum sulphate solution according to the condition of the water that is being treated in the basin; the amount of aluminum sulphate used ranges from 4 to 16 per cent. This variation in strength provides for maintaining a constant relation between the volume of water pumped out from the station and the quantity of aluminum sulphate solution used for its purification. Recording Venturi meters are used to record both the amount of water that is pumped and the volume of aluminum sulphate solution that is being delivered to the settling basin. The attendant observes the indications of these meters at specified intervals, and makes any alterations in the setting of the valves leading from the solution tanks that may be necessary to maintain the required flow of aluminum sulphate solution into the settling basin. The indications of the Venturi meter used to measure the volume of solution fed into the settling basin are checked by observing the drop of the level of the solu-

tion in the storage tanks; the volume is then calculated from a knowledge of the dimensions of the tank. The table which is reproduced below has been prepared for the guidance of the attendant, the purpose being to relieve him of the necessity of making any calculations in determining the required volume of

Fig. 1.

aluminum sulphate solution for the particular rate at which water is being pumped out from the basin.

TABLE I.

Gallons of Water per 24 hours.	Gallons of Solution per 24 hours.
10,000,000	260
11,000,000	286
12,000,000	312
13,000,000	338
14,000,000	364
15,000,000	390
16,000,000	416
17,000,000	442
18,000,000	468
19,000,000	494
20,000,000	520
21,000,000	546
22,000,000	572
23,000,000	598
24,000,000	624
25,000,000	650
26,000,000	676
27,000,000	702
28,000,000	728
29,000,000	754
30,000,000	780
31,000,000	806

When the aluminum sulphate solution is fed into the basin, the chemical reactions which take place result in the conversion of the aluminum sulphate into aluminum hydrate. This flocculent precipitate of alumina settles slowly in the basin and carries down both the impurities in suspension and those that are in solution by a process known as "adsorption." Adsorption consists of the envelopment of the impurities in the water in the alumina, in which they are carried to the bottom of the basin. The purification effected by the action of the alumina is materially aided by the removal of a considerable quantity of the suspended matter that settles to the bottom of the basin by reason of its greater specific gravity. The alumina and the impurities from the water settle out as a sludge that must be removed once a year; this is done by simply pumping it over the embankment that surrounds the basin. From 60 to 70 per cent of the impurities in the raw water are removed by the treatment in the settling basin. A good idea of the degree of purification that is effected may be gathered by looking down upon the surface of the water in the settling basin. The water over the delivery pipe is yellow and muddy, but this color changes gradually to a clear blue over the pipe at the opposite end of the basin, that carries the sedimented water away to the filters. In addition to the removal of chemical impurities, a large percentage of the bacteria in the water are also removed during the process of sedimentation.

THE FILTERS.

There are eight filters located on the second floor of the filtration plant, four on either side of the building. These filters are housed in concrete cells, one of which is illustrated in Fig. 1. The filter bed consists of gravel ranging in size from small pebbles at the bottom to a layer of fine sea sand at the upper surface. This bed

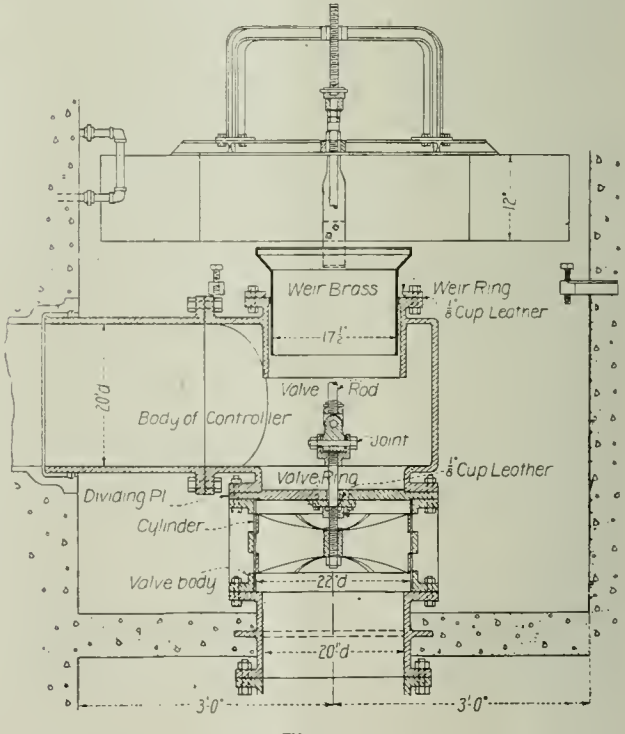


Fig. 2.

is supported by a perforated brass plate or screen at the bottom of the filter cell.

The water comes to the filters through a pipe leading out from the settling basin. This pipe runs the length of the filtration plant and has branch pipes leading to each of the filters. Modern practice requires the rate of filtration to be both rapid and con-

stant. The natural course of events, however, is for the rate of filtration to decrease as the length of time that the filter has been in operation increases. This is due to the clogging of the filter bed with a "felt" of alumina and suspended matter that has been removed from the water. To overcome this difficulty, each of the filters is equipped with a "regulator box" through which the water passes on its way to the clear well. The design of this device is shown in Fig. 2, from

Fig. 3.

which it will be seen that the water, after passing through the filter, goes through a valve and then over a circular weir down to the clear well. The openings in the valve are automatically regulated by means of a float attached to one part of the valve mechanism. As the filter begins to clog, the reduction in the flow of water lowers the level in the regulator box. This causes the float to drop, thus opening the valve wider and increasing the amount of water that flows through it and over the weir into the clear well. In starting a new filter, the desired rate of flow is secured by regulating the perpendicular distance between the lower edge of the float and the lip of the weir. The lower the weir is set, the faster the water flows over it; this causes the level at which the float stands to drop and opens the valve sufficiently to maintain this rate of flow. The regulation of the relative position of the float and the weir is accomplished by means of the hand-wheel seen just behind the recording gauge in Fig. 1. This wheel is mounted on a rod that has two threaded portions—one right hand and the other left—that run through the central hubs in the spiders in the float and the weir. By turning this hand-wheel, the weir and float may be made to either approach or move away from each other as desired.

The two doors in the front of the cabinet in Fig. 1 give access to the regulator box. On top of the cabinet, there will be seen a pressure gauge and a recording gauge that accounts for the volume of water delivered to the clear well. It will also be seen that there are seven small levers that rotate over graduated dials. These levers actuate three-way cocks which, in turn, operate the various hydraulic gates that control the flow of water to and from the filter beds. There is one of these cabinets for each of the eight filters in the plant.

A filter is operated for a period of eight hours, after which it requires cleaning. The first step in the cleaning process consists of blowing air up through the filter to break up the felt of alumina and insoluble impurities from the water that has collected on the filter bed. The air for this purpose is delivered to the filter through the black goose-neck pipe which appears above the wall of the cell shown in Fig. 1. The lower ends of these pipes branch out into a number of perforated arms that reach to all parts of the filter beds at a level close to the bottom of the gravel. The air is supplied by B. F. Sturtevant blowers that are driven by direct connected Pelton water wheels. Air is blown through the filter for three minutes, and at the end of that time, the felt that had formed on the bed has become thoroughly broken up and is suspended in the water standing in the cell. Water is then forced up through the filter bed for from eight to twelve minutes—from forty thousand to sixty thousand gallons being used—and this water carries away the dirt with it through troughs leading to the sewer.

THE CLEAR WELL.

To go back to the purified water; that passed through the filters; after going over the weirs into the regulator boxes, it descends into the clear well. This clear well is a concrete basin which occupies the entire space under the filtration plant. A pipe leads from the clear well to the suction basins from which the water is pumped out into the mains. The last step in the process of purification consists of adding hypochlorite of lime to kill the small number of bacteria that still remain in the water. The solution used for this pur-

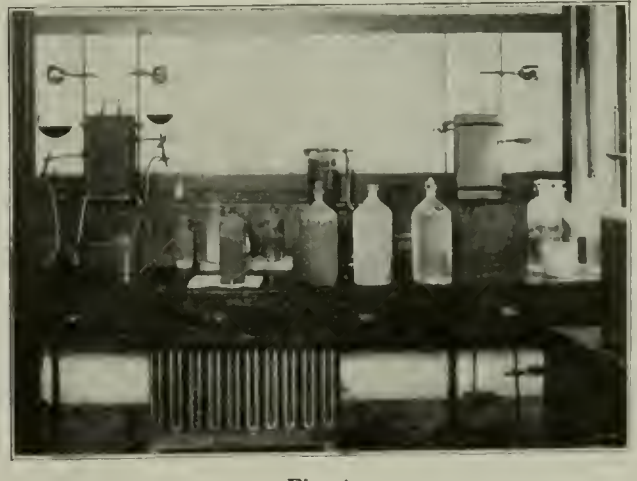


Fig. 4.

pose is mixed in a tank located on the third floor of the filtration plant, and is introduced into the water as it flows through the pipe connecting the clear well with the suction basins. The strength of the solution is such that from 5 to 12 lbs. of the hypochlorite of lime

are added to each million gallons of water, the amount depending upon the number of bacteria present. It was formerly the practice to introduce the hypochlorite solution into the filters, but it has been found that a better distribution is secured by using the present method. Where there is a slight excess of hypochlorite of lime present in the water, practically complete sterilization is secured.

THE PUMPING STATION.

The equipment of the pumping station consists of three Allis-Chalmers, vertical pumping engines and one horizontal Worthington pumping engine. The capacities of the three Allis-Chalmers units are twenty million, eighteen million, and fifteen million gallons respectively, while the Worthington unit has a capacity of ten million gallons per twenty-four hours. This gives the plant a total pump capacity of 63,000,000 gals. per 24 hours, but a heavy reserve capacity is provided for as the output does not exceed 30,000,000 gals. per 24 hours at the present time. The twenty million gallon pump is a new unit which has only recently been placed in operation. The engine is of the triple expansion type. This unit is supplied with steam from a battery of five hundred horsepower Sterling water tube boilers, which are operated in connection with Green fuel economizers. The other pumping units in the plant are supplied with steam from two batteries of Aultman & Taylor water tube boilers. The boiler room is housed in a separate building adjoining the pumping station, and all of the boilers are hand stoked.

THE LABORATORY.

The laboratory maintained at the filtration plant is completely equipped for conducting chemical and bacteriological examinations of the water. The routine work may be briefly outlined as follows: Every eight hours, samples of the raw, sedimented and filtered water are taken, on which counts of the total number of bacteria are made. The usual Petrie dishes are employed for this purpose, the culture from one cubic centimeter of water being allowed to develop for 48 hours at a temperature of 20° C. before the count is made. The regular form of subdivided disk is used for making the count, the disk being placed over the Petrie dish in the customary way. The practice in this laboratory is to make a series of ten counts of the bacteria under ten spaces chosen at random. The results of these counts are then averaged to obtain the mean result, thus reducing the probability of personal error. Fig. 3 shows a view of the bacteriological laboratory in which the apparatus for making counts of the bacteria in the water will be seen.

Every morning at 8 o'clock, samples of the water are tested for the presence of B coli-communis. Ten cubic centimeters of water are used for this purpose, the culture being made in ox-bile in the regular form of fermentation tubes. One per cent of sugar—either lactose or dextrose—is added to the ox-bile to facilitate the fermentation.

Once a week, samples of water are taken from all of the district reservoirs and all of the district offices. These twelve samples are subjected to the bacteriological examination outlined above. At this point, it will be of interest to compare the number of bacteria present in the river water and in the purified water sent out from the plant. The raw or river water averages three thousand bacteria per cubic centimeter, while the purified water pumped into the mains only carries an average of twenty bacteria per cubic centimeter. This means that an efficiency of approximately 99.4 per cent has been attained for the bacteriological purification.

Every two weeks the water is subjected to a complete sanitary analysis, in accordance with the standard methods now in vogue. Tests are also made for color, the filtered water being compared with standard reference samples. Another important test is that of determining the presence of a slight excess of hypochlorite of lime or "bleach" in the water. An excess of hypochlorite of lime is a practical guarantee of the death of all bacteria in the water but it is important that the excess shall be very small. The method of conducting this test consists of acidifying the water with acetic acid; a little potassium iodide solution is then added. If there is an excess of hypochlorite of lime present in the water, the chlorine will replace the iodine in the potassium iodide. By adding a little starch solution, the familiar blue coloration will then be produced by the reaction between the free iodine and the starch. The amount of excess hypochlorite can be roughly estimated from the intensity of the coloration produced by the iodo-starch reaction, and this serves as a guide in adding the hypochlorite of lime solution to the water. The bottle standing on the white paper in Fig. 4 gives an idea of the method followed in making this test. The three bottles to the right contain raw, sedimented and filtered water respectively. These samples afford a good idea of the degree of purification that is effected, also of the stages of the process in which this purification takes place.

Sheffield steel experts are awaiting with considerable interest further information concerning tests which, it is stated, have been applied with some success to armor plates manufactured by a new process which, the inventor claims, renders them capable of resisting projectiles of the highest power. The inventor is William Henry Worrall, of Sheffield. He states that the new armor plate does not at all rely upon any new ingredient for its increased resisting power, but that this is obtained as the result of a different process of hardening, largely secured by the welding or bonding of four or six sheets of metal into one plate, instead of molding the plate as a whole in one ingot. The main object is to effect a thorough homogeneous hardness. This, it is said, will permit of ironclads being as efficiently protected with much thinner and lighter plates than is at present the case.

THE HYDROGENATION OF OILS.*

By CARLETON ELLIS.

The treatment of unsaturated oily bodies with hydrogen to obtain saturated derivatives is of great scientific and technical interest. In the fat industry a most fascinating problem has been that of the conversion of oleic acid or olein into stearic acid or the corresponding glyceride.

Oleic acid and hydrogen combine, molecule for molecule, to yield stearic acid according to the reaction:

$$C_{18}H_{34}O_2 + H_2 = C_{18}H_{36}O_2.$$

Thus 282 lbs. of oleic acid require 2 lbs. (or about 0.7 per cent) of hydrogen for the production of 284 lbs. of stearic acid, and similarly the transformation of olein into stearine requires the use of about 0.68 per cent hydrogen.

One thousand cubic feet hydrogen weigh approximately 5.6 lbs., hence a pound of olein calls for a little over 0.1 of an ounce of hydrogen, equivalent to approximately 2500 cu. ft. of hydrogen per ton (of 2,000 lbs.) of olein. Thus by weight only a relatively small quantity of hydrogen is needed, while by volume the amount required, of course, is considerable.

Many attempts to hydrogenate oleic acid have been made. Reviewing this subject in 1897[1] Lewkowitsch refers to the ease with which the lower members of the oleic series are converted into saturated acids and states that "oleic acid itself resists all attempts at hydrogenization," further remarking that he had "carried out a large number of experiments in this direction under most varied conditions, but hitherto all of these gave negative results."

Prior to this, however, Goldschmidt, in 1875,[2] had reduced oleic acid by means of hydriodic acid and amorphous phosphorus at 200-210° C. This presumably let to the attempted commercial development of a process by de Wilde and Reychler[3] involving heating oleic acid to 280° C. with 1 per cent of iodine, adding and melting therein a certain quantity of tallow soap, and then boiling with acidulated water. The product was then distilled and the iodine, in part, recovered from the pitch. The yield of stearic acid or saturated fat is stated to be approximately 70 per cent of the theoretical. Only about two-thirds of the iodine could be recovered, so the process apparently did not find technical use.[4] Should the much lauded method of treating kelp, primarily for obtaining potash salts, come into use, a cheap supply of iodine would be available, which might then make the Wilde and Reychler process of some technical interest.

Chlorine in lieu of iodine has been tried, but great difficulty has been experienced in securing an autoclave of resistant material. Imbert[5] recommends using quantities of chlorine and alkali exactly calculated on the iodine number of the fatty acid and operating at a temperature of 120° to 150° C. and pressure of about five atmospheres for a period of six hours.

Zürrer[6] chlorinates the fatty acid and then heats with water in the presence of a finely divided metal, as zinc or iron. Lewkowitsch alleges that the treatment of monochlor-stearic acid in this manner causes a reversion to oleic acid.

Tissier, in 1897,[7] lays claim to a process for the reduction of oleic acid by nascent hydrogen. Powdered metallic zinc is placed in an autoclave, water and the fatty material containing olein introduced and treated under pressure.

Under the circumstances, the glyceride is hydrolyzed to fatty acid and glycerine, and according to Tissier nascent hydrogen is evolved by virtue of the finely divided metal and reduces the oleic to stearic acid. Freundlich and Rosauer[8] claim the Tissier process to be inoperative.

The conversion of oleic acid into palmitic and acetic acids by means of caustic potash in accordance with the Varentrapp reaction[9] has not proved to be of much commercial significance, although it appears that certain firms have been making use of the process in a limited way.

The Schmidt zinc chloride process[10] involves heating oleic acid and zinc chloride at exactly 185° C. while interaction is taking place. "Deviation from this point leads to an increase of liquid substance. Unfortunately, the solid candle material must be distilled and the considerable proportion of β-hydroxy-stearic acid (melting point 82° C.) in the crude product is seriously diminished by the partial conversion of this acid into oleic and iso-oleic acids. Thus, from a candle-maker's point of view, a substance of high melting point is rendered practically valueless. Schmidt's process was tried on the large scale in an Austrian candle works. The quantity of liquid *unsaponifiable* substance obtained was, however, so large that commercial success was out of the question."

Many processes have been proposed based on the well-known action of sulfuric acid on oleic acid. Hydroxy-stearic acid is obtained by steaming the product. It would lead us too far from the present subject to enter into any further discussion of these reactions.

PROCESSES INVOLVING APPLICATION OF ELECTRICITY.

In 1886, Weineck[11] called attention to the possibility of electrolytic addition of hydrogen to oleic acid. Kuess[12] later attempted to apply the electric current in the steam distillation of fatty acids.

In patents taken out by Magnier, Bragnier and Tissier,[13] the fatty material is acidified with sulfuric

*Presented before the New York section of the Society of Chemical Industry, Nov. 22, 1912, and reprinted in the Journal of Industrial and Engineering Chemistry.

[1] J. S. C. I., 389 (1897).
[2] Sitz. b. d. Wiener Akad. d. Wiss., 72, 366.
[3] Bull. Soc. Chim. [3], 1, 295 (1889).
[4] Chem. Ztg., 595 (1889).
[5] U. S. patent No. 901,905, of Oct. 20, 1908; see also Bull. Soc. Chim., 695, 707 (1899).
[6] German patent No. 62,407, of Aug. 8, 1891.
[7] French patent No. 263,158, of Jan. 16, 1897.
[8] Chem. Ztg., 566 (1900).
[9] J. S. C. I., 98 (1883), 200 (1884).
[10] Lewkowitsch, "Oils, Fats and Waxes," p. 664.
[11] Osterr. Privil., 10, 400 (July 19, 1886).
[12] Chem. Ztg., 618 (1896).

acid, whereupon the acidified mass is mixed with 5 or 6 times its weight of water and then, under a pressure of 5 atmospheres, is subjected to the action of an electric current, which generates hydrogen in a nascent state.

An interesting method of converting oleic into stearic acid is that comprised in the Hemptinne electric discharge process. The method is carried out by interposing a thin layer of the oil in the path of an

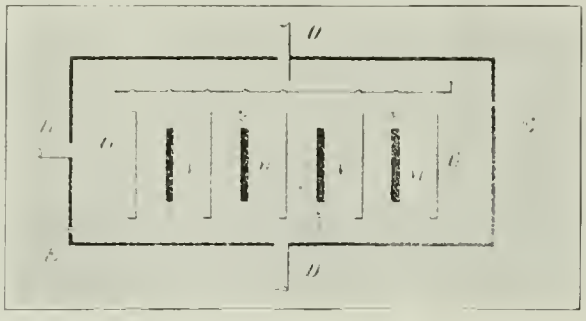


Fig. 1.

electric discharge, while bringing hydrogen into contact with the oil.[14]

Figure 1 shows the arrangement of apparatus for this purpose. The conversion is effected in a chamber having an inlet pipe, H, furnishing hydrogen under constant pressure. Oleic acid is supplied by a pipe, O, to a sprinkling device which discharges the acid onto a system of parallel plates consisting of the glass plates G and alternately the metal plates M, N. The metal plates M are connected to one pole, the others, N, being connected with the other pole of a source of electricity. As the oil passes over the plates the electrical discharge causes conversion of some oleic acid into stearic acid, and analogous compounds having melting points in the neighborhood of 69° C.

Hemptinne prefers to work at pressures less than atmospheric. The yield is lower at atmospheric pressure. By treatment in this manner it is not difficult to secure a yield of 20 per cent of stearic acid. Repeated treatment permits even up to about 40 per cent yield. Here, as so often elsewhere, the effect of mass action becomes manifest, and as the content of stearic acid increases the speed of reaction greatly decreases. Much better results are obtained by saturating to the extent of about 20 per cent, removing the stearic acid by pressing, when the oil of reduced stearic acid content is again subjected to the electric discharge, and a further 20 per cent yield obtained. The oleic residue contains liquid condensation products amounting to about 40 per cent of the total weight. It is stated that the presence of these bodies does not impair the market value of what some one has termed "electrocuted" oleic acid.

"J. Petersen[15] also endeavored to reduce oleic acid to stearic acid by allowing an electric current to act between nickel electrodes on an alcoholic oleic acid solution, slightly acidulated with sulfuric acid or preferably with hydrochloric acid. But the yield of stearic acid was small, even under the most favorable conditions, and did not exceed 15 to 20 per cent."

Petersen also endeavored to reduce sodium oleate in aqueous or alcoholic solution to the stearate. No satisfactory results were obtained.

C. F. Böhringer and Sohne[16] obtained by the same method much better results when using as cathodes metallic electrodes, which were covered with a spongy layer of the same metal. They recommend as cathodes platinized platinum, and also palladium electrodes covered with a spongy layer of palladium-black. Nickel electrodes are not as effective.

Kolbe[17] in 1871 states that Saytzeff reduced nitrobenzol to aniline by passing the vapors of the former, mingled with hydrogen, over palladium-black.

About twenty-five years later Sabatier and Senderens began their classic study of nickel and other metallic catalyzers.

The work of Sabatier and Senderens laid the foundation for the present processes of hydrogenation of oils. Their work is so well known that it is needless to discuss it here.

Figure 2 shows apparatus used by these investigators in the hydrogenation of bodies capable of vaporization. In this apparatus, 1 is a hydrogen generator; 2 and 3 are wash bottles, and 4 is a vaporizer containing the substance to be converted into a vapor; 5 is a hydrogen chamber containing nickel catalyzer and heated by an oil bath; 6 is a condenser.

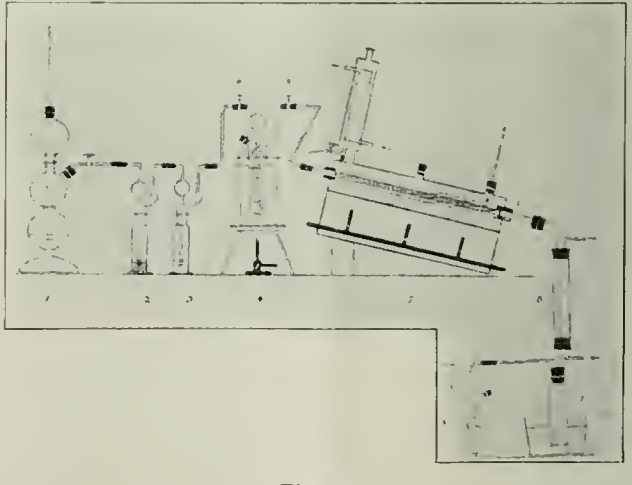


Fig. 2.

While a good deal of work has been done on the hydrogenation of fatty oils, the literature on the subject is very meagre indeed, and only through the patents which have been issued can we gather from any published records much that is enlightening as to dedevlopments in this industry. The patents concerned with the matter have, moreover, been subjected to a great deal of scrutiny, because of the alleged basic

[14] Eng. patent No. 3,363, 1900; German patent No. 126,446, of Oct. 3, 1899, and additional German patent No. 132,223.
[14] U. S. patent No. 797,112, of Aug. 15, 1905.
[15] Z. Elektrochemie, 549 (1905).
[16] German patents Nos. 187,788, 189,332, 1906.
[17] J. prakt. Chem., [2] 4, 418 (1871).

character of certain of them. For these reasons the following discussion pertains very largely to processes which have been covered by patents in this country or abroad.

(NOTE.—The illustrations herein are largely derived from the drawings of patent records or have been prepared from written descriptions. All details deemed unnecessary in the portrayal of the essential features

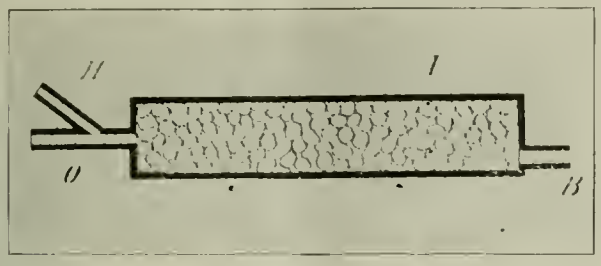


Fig. 3.

of these processes have been omitted. The original records should, of course, be consulted for details.—AUTHOR.)

A German Patent, No. 139,457, of July 26, 1901, to J. B. Senderens, is probably the first patent record having to do with the reduction of organic bodies by hydrogen in the presence of nickel catalyzers. This patent is for the production of aniline from nitro-benzol and involves passing the latter body in the form of a vapor over heated nickel, copper, cobalt, iron, or or palladium in the presence of hydrogen. The hydrogen may be in the pure state or in the form of water-gas.

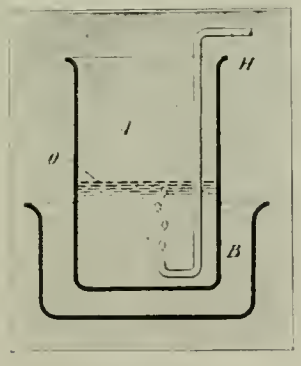


Fig. 4.

The first disclosure of the possibility of hydrogenation of oils in a liquid state apparently comes from Le Prince and Siveke.[18] In England a corresponding patent (No. 1515, of 1903) was issued to Normann[19] and the latter patent has become widely known because of its alleged fundamental character.

Normann states that he may carry out the hydrogenation of oils by treatment either in the form of vapors or as liquids. In the former case the fatty acid vapors together with hydrogen may be caused to pass over catalytic material carried by a pumice stone support. This may be represented by Fig. 3, in which A is a bed containing granular pumice coated with a metal catalyzer. O is an inlet for oil *vapors* and H is an inlet for hydrogen. The mixture passes through the tube A and the converted material is withdrawn at B. Normann notes, however, that it is sufficient to expose the fat or fatty acid in a liquid condition to the action of hydrogen and the catalytic substance. He states, for instance, if fine nickel powder obtained by the reduction of nickel oxide in a current of hydrogen is added to oleic acid, the latter heated over an oil bath and a strong current of hydrogen caused to pass through it for a considerable time, that the oleic acid may be completely converted into stearic acid.

Fig. 4 shows very simple apparatus, such as might have been used by Normann to this end. A is a vessel containing oil, O, in which fine particles of nickel are suspended while a strong current of hydrogen from

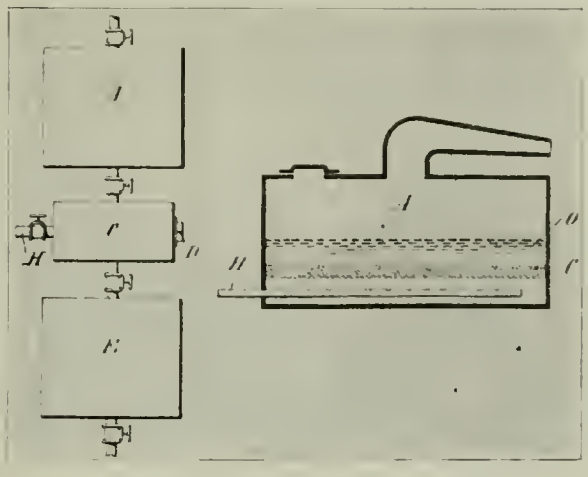


Fig. 5. Fig. 6.

the pipe H affords the hydrogen requisite for reduction of the oil. By this means Normann treated the fatty acid of tallow having an iodine number of 35 and melting at about 46, thereby converting it into a body of improved color having an iodine number of about 10 and a melting point of about 58. Normann also states that commercial gas mixtures, such as water-gas, may be used in lieu of pure hydrogen.

The disclosures of the Normann patent are, however, rather meagre and hardly can be considered to comprehensively traverse the difficulties encountered in the practical hydrogenation of oils in a liquid state.

Dr. David T. Day, of Washington, has brought out a process,[20] in which he treats, not fatty oils, but hydrocarbon oils, with hydrogen in the presence of what he terms a porous absorptive substance, mentioning palladium-black, platinum sponge, zinc dust, fuller's earth and other clays. Fig. 5 shows one method proposed by Day to this end.

The upper chamber A is filled with hydrocarbon oil, and porous absorptive material such as palladium-black is introduced in the intermediate chamber C by

[18] German patent No. 141,029, of Aug. 14, 1902, Herforder Maschinenfett und Oel Fabrik.

[19] This English patent is owned by a large soap manufacturing house in England and it is reported they allege the patent in that country to be fundamental and controlling for the hydrogenation of fatty oils generally. They are offering rewards for information as to the secret and unauthorized use of the process and it is said already to have started litigation.

[20] U. S. patent No. 826,089, of July 17, 1906.

way of the plugged orifice D. Any air present in C may be expelled by flushing out with hydrogen or an indifferent gas. Hydrogen is then admitted by the pipe H until the porous material has absorbed its full quota. The hydrogen gas may be admitted under a pressure of 100 pounds or more to the square inch.

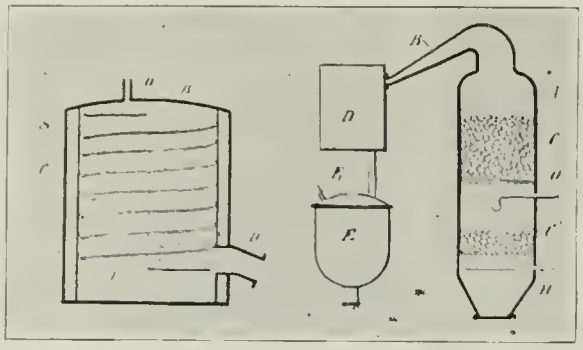


Fig. 7.

Fig. 8.

When the porous material in C has become properly charged with hydrogen, the oil is allowed to run from the chamber A through the chamber C into the collecting chamber E, hydrogen being introduced as required by the pipe H.

In the place of hydrogen, Day states that ethylene or other hydrogen carrying gas or vapor may be employed. By this treatment the disagreeable odor of hydrocarbon oil is in great part removed and the burning qualities of the oil improved. When palladium black is used it is recommended that a proportion of one-half ounce to the gallon of oil be taken.

Figure 6 shows a modification of Day's process. A is an oil still, in the lower part of which the perforated pipe H serves for the admission of hydrogen. Palladium-black or other porous absorptive material forms a layer, C, on a screen above the hydrogen inlet. O shows the charge of oil. In operating this apparatus the layer of material C is first charged with hydrogen and then oil run into the still. Distillation is carried out while hydrogen gas is being forced through the absorptive material and oil.

A peculiar manner of treatment has been shown by Schwoerer,[21] which will be made clear by Fig. 7. The receptacle A, which is heated by the steam jacket S, is provided with what Schwoerer calls a helical pan, shown at B. The underside of the pan carries a layer of nickelized asbestos. O is an inlet for oil and hydrogen, and D an outlet for the treated material.

Schwoerer states that he first mixes fatty acid and hydrogen by atomizing the oil with a jet of superheated steam in the presence of hydrogen and conducts this mixture through the pipe O, into the chamber A. The temperature maintained in the apparatus is from 250 to 270° C. Vapors of oleic acid come in contact with the layer of catalyzer on the underside of the helical pan and are converted into stearic acid. The product collects, more or less, in the gutter of the helical pan and is removed at D.

[21] U. S. patent No. 902,177, of Oct. 27, 1908.

The repeated caution given by Sabatier to bring in contact with the catalyzer only the *vapors* of the material, doubtless led Schwoerer to devise this form of apparatus.[22]

Bedford, presumably with the same caution of Sabatier in mind, discloses, in U. S. Patent No. 949,954, of Feb. 22, 1910, a process which also has to do with vaporization of the oily material. Fig. 8 shows the Bedford apparatus. A still or tower, A, carries two beds of catalyzer, C and C'. This is said to be preferably nickelized pumice. By means of hydrogen under pressure, oleic acid is sprayed from the pipe O, onto the catalyzer bed C'. Hydrogen is admitted through the pipe H. A temperature of about 200° C. and a diminished pressure of about 50 to 100 mm. is maintained in the still or tower A. The vapors of oleic acid mingled with hydrogen pass through the second catalyzer bed C, where more or less conversion occurs, then pass to the condenser D, and finally collect in the receptacle E. F is a connection to a vacuum pump.

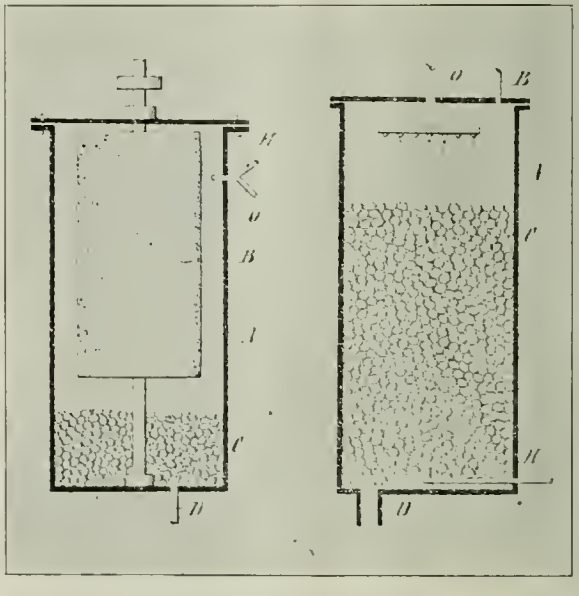


Fig. 9.

Fig. 10.

Neither this process nor that of Schwoerer is broadly applicable to the treatment of glycerides as these cannot be vaporized without undue decomposition.

Erdmann has taken out a German Patent No. 211,669, of Jan. 19, 1907, involving passing an oil as spray or mist into a chamber containing nickel catalyzer supported on pumice and the like. Fig. 9 probably indicates one form suggested by Erdmann, who, by the way, does not show any drawings in the patent. The chamber A has a rotatable cylinder, B, which is coated with nickel catalyzer. In the bottom of the recep-

[22] Sabatier and Senderens, Annales de Chimie et de Physique, [8] 4, 335 (1905), state that "Le métal ne soit jamais mouillé par un afflux excessif du liquide que l'on traite, ou a la suite d'un abaissement accidentel de la temperature du tube." They further say that in the preparation of cyclohexanol and its homologues from phenol or cresol, at a temperature but slightly above the boiling points of the latter bodies, sometimes by their condensation, the nickel becomes moistened and immediately becomes almost inactive, due, no doubt, to the surface becoming permanently changed in character by contact with the liquid phenol or cresol.

tacle is a quantity of nickelized pumice. Oil enters at O and is atomized by hydrogen entering at H. The atomized mixture impinges upon the rotating cylinder B, then passes through the bed C, the oil being drawn off at D. The excess of hydrogen is presumably vented in the upper part of the apparatus.

A second modification (Fig. 10) involves a tower, A, filled with catalyzer C, which may be in the form

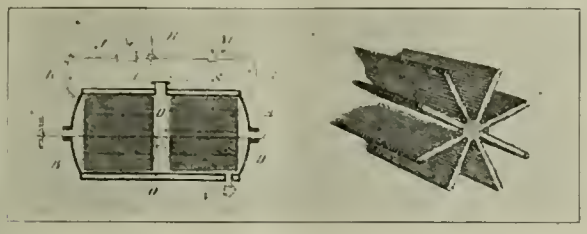


Fig. 11. Fig. 12.

of nickel supported on coarse fragments of pumice. By the pipe O, oil is admitted to the chamber in an atomized or finely divided state. Hydrogen enters by the pipe H. Erdmann states that the temperature of treatment should be from 170 to 180° C. The treated oil is drawn off at D while the excess of hydrogen passes away at B .

In a supplemental patent No. 221,890, of Jan. 19, 1907, Erdmann recommends the steam distillation from the reaction chamber of the saturated product under diminished pressure.

Vereinigte Chemische Werke A. G.[23] make use of palladium catalyzer precipitated on an indifferent body as a carrier and recommend as carriers finely divided metals which do not have anti-catalytic properties, also metal oxides and carbonates. Under these circumstances it is stated that one part of palladium is sufficient to convert in a few hours 100,000 parts of oily material to a firm mass. They recommend the use of a hydrogen pressure of two to three atmospheres and a temperature somewhat above the solidification point of the saturated fat. They caution against arsenic, hydrogen phosphide and sulphide, liquid hydrocarbons and carbon bisulphide, chloroform, acetone and free mineral acids as being destructive to the activity of the catalyzer.

Kayser[24] describes a process of treating oil with metallic catalyzer consisting in mechanically agitating the oil and catalyzer in the presence of hydrogen, preferably under pressure. One form of the apparatus indicated by Kayser for this purpose is diagrammatically represented by Fig. 11.

Here A is a closed horizontal cylindrical vessel in which is a paddle wheel D, made up of blades carrying wire gauze. The paddle wheel is rotated by a driving gear at B. In the upper part of the tank is an inlet for charging oil and presumably also catalyzer, the oil being admitted to the tank in an amount sufficient to fill to perhaps one-fourth or one-fifth the entire capacity. Hydrogen is admitted at H and passes by the three-way cock I, to the compression pump J, going from there to the treating receptacle. At the opposite end of the tank is an exhaust pipe, L, carrying a blow-off valve, M, for the purpose of venting the unabsorbed hydrogen. The temperature of treatment is stated to be about 150 to 160° C. Although the claims call for the use of hydrogen under pressure, no working pressures are specified. Fig. 12 shows diagrammatically one form of construction of the screen-covered paddle wheel used by Kayser.

In another U. S. Patent (No. 1,008,474, of Nov. 14, 1911), Kayser sets forth the use of an inert pulverulent material such as kieselguhr as a carrier for the nickel catalyzer, he apparently having determined, as did Sabatier and others, that hydrogenation is more rapid or complete when a carrier for the catalyzer is used; and he claims the process of hydrogenating oil involving agitation of a metallized inert pulverulent carrier with a fatty oil in the presence of hydrogen. It is commonly understood that the Kayser process is in operation on the large scale in this country.

Two patents relating to the spraying of oil into a chamber containing compressed hydrogen have attracted some attention abroad. One of these is English Patent No. 7,726, of 1910 to Testrup and the other is to Wilbuschewitch which finds its counterpart here in U. S. Patent No. 1,024,758, of April 30, 1912. Fig. 13 shows the elements of the Testrup process.

Oil and catalyzer are pumped through the pipe O, into the tank A, and hydrogen is admitted by the pipe H, to furnish a gas pressure of say 15 atmospheres.

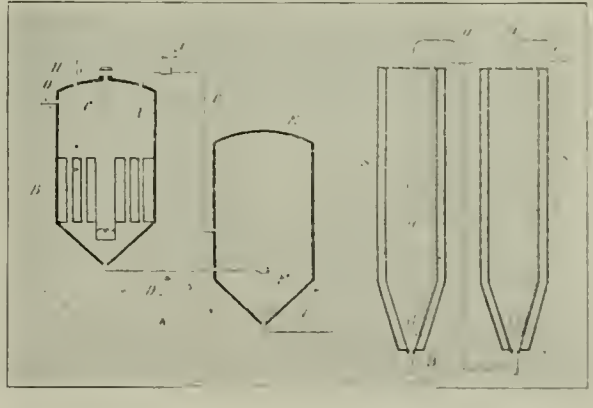


Fig. 13. Fig. 14.

The tubes B are heated by steam and the stirrer C circulates the oil and catalyzer in the tank A, until the oil has become heated and presumably somewhat hydrogenated. The oil is allowed to pass into the adjacent tank E, entering this tank by the spray nozzle F. Hydrogen gas is admitted to the tank E, from the tank A, so as to afford a pressure of, say 12 atmospheres in the tank E. A series of tanks may be arranged with a constantly decreasing pressure so that the differential pressure enables the spraying of the oil from tank to tank. Testrup states that spraying

[23] German patent No. 236,488, of Aug. 6, 1910; also English patent No. 18,642, of 1911.

[24] U. S. patent No. 1,004,025, of Sept. 26, 1911.

the material ten or fifteen times is sufficient to bring an oil of an iodine number of 110 down to an iodine number of 50.

As catalyzer, Testrup recommends finely divided palladium or preferably nickel, the latter being two to three per cent, by weight of the oil. As a treating temperature 160 to 170° C. is mentioned.

The Wilbuschewitch patent itself details a rather complicated system and Fig. 14 shows only what appears to be the essential features of the treating apparatus. Several tanks or autoclaves are connected as shown at A and A', oil entering the top of the tank

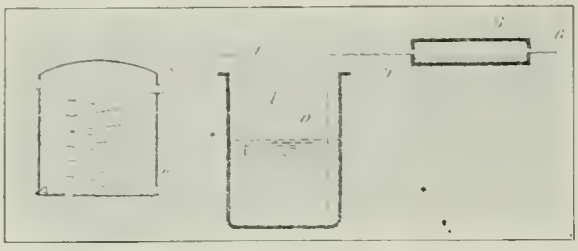


Fig. 15.

Fig. 16.

A by the pipe O, to form a spray which in descending meets an upward current of hydrogen entering by the pipe H. The oil is drawn off through the pipe O', and sprayed into the tank A'. This time it meets a current of hydrogen represented by the excess of hydrogen coming from the tank A. The treated oil is drawn off and may be centrifuged to remove the catalyzer. A pressure of nine atmospheres is recommended and the pressures may be varied in the different tanks.

Of the Wilbuschewitch process Goldschmidt[25] states that the high hydrogen pressures employed enable the reaction to take place quickly at temperatures between 100 and 160° C., so that the fat is not likely to be injured by the temperature to which it is subjected. It should be stated that several years previous to the date of the Wilbuschewitch patent, Ipatiew had noted and carefully studied the action of increased pressure.[26]

Bedford and Williams[27] have brought out an interesting process represented by U. S. Patent No. 1,026,339, of May 14, 1912. Fig. 15 shows the apparatus indicated by Bedford and Williams for carrying out the process. Oil is placed in the receptacle A, which is heated by a steam coil, S. Metallic *oxide* catalyzer is added, about 1 per cent being recommended, and hydrogen and oxygen or air is introduced by the pipe H. As a catalyzer, nickel oxide (previously used by Ipatiew) is recommended and instead of the customary hydrogenating temperature of 150 to 170° C., a temperature of about 250° C is employed. While hydrogen alone may be used for the purpose, the inventors recommend and claim treatment of the oil with a mixture of hydrogen and oxygen to form hydroxy fatty acids or their glycerides.

Shukoff[28] claims the process of hydrogenating oils by means of nickel derived from the decomposition of nickel carbonyl. Nickel carbonyl may be obtained from reduced metallic nickel by passing carbon monoxide over it at a low temperature. Nickel carbonyl is soluble in oil and is very readily taken up by gases. On heating to a temperature of 200° or so, the carbonyl is decomposed, setting free, in a nascent state, metallic nickel which acts as a catalyzer. Shukoff makes use of this reaction of nickel carbonyl by the method indicated by Fig. 16. Carbon monoxide is passed by the pipe G, into the tube B, containing finely divided nickel and the nickel carbonyl formed is conducted to the oil O, which is heated to about 180°. After sufficient nickel catalyzer has formed in the oil, the carbon monoxide stream is cut off, the temperature raised to 220 or 240° C. and hydrogen gas introduced by the pipe H, to bring about hydrogenation.

Day has taken out U. S. Patent No. 1,004,632, of Oct. 3, 1911, supplementing his earlier patent on the treatment of hydrocarbon oils with hydrogen. In the present instance tubes packed with catalyzer are placed in an oil still in such a manner that vapors from the oil may pass through the catalyzer tube in conjunction with hydrogen, while being superheated by exterior contact of the tubes with boiling oil.

An English Patent, No. 23,997, of 1909, to Phillips

Fig. 17.

Fig. 18.

and Bultell, claims to convert mineral oils into oils of lower specific gravity by heating with hydrogen in the presence of nickel or other catalytic agents. They state that the mixture of oil, gas and catalyst may be blown into a heated cylinder and the jet given a gyratory motion either by means of a nozzle revolving about its axis, or by injecting the mixture tangentially to the periphery. In the latter case they state that the cylinder may have an axial core.

The firm of H. Schlinck & Co., of Hamburg, Germany,[29] hydrogenate oil by passage through a centrifuge, the drum of which carries a porous lining of palladium catalyzer which offers a frictional resistance to the passage of the oil. Fig. 17 shows a centrifugal drum, *a*, which is closed at the top and can be heated.

[25] Chem. Ztg., 945 (1912).

[26] Rumor has it that the processes of Testrup and Wilbuschewitch were so much alike that during the prosecution of their patent applications before the English Patent Office they concluded to unite interests and that subsequently they sold the rights in England to a soap manufacturer who, it is alleged, proposes to contest the claims of the present owners of the Normann patent as to the alleged basic nature of the latter.

[27] It is reported that in England some of the independent soap manufacturers have taken over this patent of Bedford and Williams and also the Erdmann rights. The Bedford and Williams process does not seem destined to be of great service in connection with the manufacture of edible fats, in part owing to the high temperature employed. It is questionable whether or not working with a mixture of hydrogen and oxygen in the presence of a catalyzer might not at times afford conditions leading to explosions.

[28] German patent No. 241,823, of Jan. 18, 1910. See also H. Kamps, Belgian patent No. 246,975, Seifensieder Ztg., 1339 (1912).

[29] English patent No. 8,147, of 1911.

Oil and hydrogen are introduced through the pipe *b*. Openings are provided in the walls of the drum in which is placed rough or porous material covered with precipitated palladium. Several drums may be arranged in series through which the oil may be caused to progress until sufficiently hydrogenated.

Ellis[30] uses a stationary catalyzer, filling tubes with the material in granular form and allowing oil to flow through the tubes while passing hydrogen in an opposite direction. Fig. 18 shows a three-section apparatus with the catalyzer tubes T, T^1 and T^2, heated by

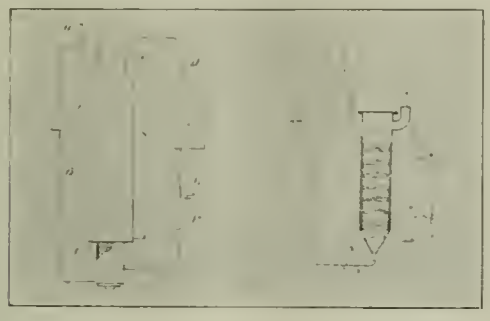


Fig. 19.

Fig. 20.

the jackets S S. Oil from tank O flows through the apparatus while hydrogen, admitted by the pipe H, passes through in an opposite direction. The arrangement permits of differential heating so that, for example, the oil may be heated to a temperature corresponding to its particular degree of hydrogenation at any given point, enabling a hydrogenated product free from burnt odor to be obtained. Fig. 19 shows a vertical form of apparatus, the catalyzer being shown at C in the tube A. Oil is introduced by the Pipe O, and passes into the tube or cylinder A. The pump P causes oil to circulate from the top to the bottom of the apparatus through the pipe B. Hydrogen gas admitted at H is pumped into the bottom of the cylinder A, and the excess is withdrawn at the top by the pipe D, passing through the drier E, and back into the treating cylinder. Oil may be continuously fed through the pipe O, in the upper part and the treated product withdrawn at the same rate at the lower part of the apparatus.

In Ellis' Patent, No. 1,040,531, of Oct. 8, 1912, the catalyzer is placed in trays or baskets as shown by Fig. 20 at C. The oil travels in a cyclic path downwardly through several layers of catalyzer, and hydrogen gas passes in an opposite direction. Separation of the catalyzer in layers in this manner enables the hydrogen to pass more uniformly through the catalyzer bed. If the catalyzer forms a bed of considerable depth and width, the gas in taking the path of least resistance is liable not to come in contact with some parts of the bed.

The activity of a properly made catalyzer is oftentimes surprising. In the case of a stationary catalyzer we have noted instances of hydrogenation where oil is converted into a hardened fat by momentary contact with the catalyzer.

Recently when using a new type of catalyzer we started to pass oil through the catalyzer tube and found hydrogen to be absorbed so vigorously by the oil that instead of passing off through an oil seal at the lower end of the inclined catalyzer tube, the oil, curiously enough, was impelled against the strong current of hydrogen passing through the horizontal tube, rushing through it to the point indicated by the hand of the operator and there solidifying actually being well hydrogenated from its momentary passage through the apparatus. A peculiar feature was the advance of the oil from the tube containing catalyzer far into the tube through which only the hydrogen was entering the apparatus. The travel of the oil along the hydrogen supplying pipe in opposition to a rapid current of hydrogen, indicates the possibility of hydrogenating in a very short time, provided a catalyzer of a high degree of activity is secured.

On the other hand, some catalyzers of the nickel and cobalt type when first brought into contact with oil and hydrogen show for a time a marked degree of sluggishness, but after a period, usually ranging from one to three hours, their activity rather suddenly augments and thenceforth remains apparent for a long period. This sluggishness should not be confounded with the seeming initial inactivity in the hydrogenation of oils containing considerable linolein or other highly unsaturated bodies. In such cases the rate of "hardening" (increase in melting point) is slow at first and later progresses more rapidly. Hydrogenation, in some cases at least, apparently proceeds

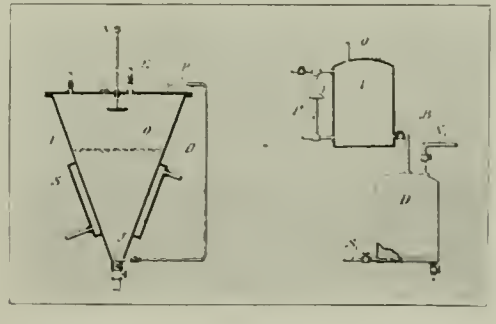


Fig. 21.

Fig. 22.

selectively with initial formation of olein from linolein. Later the olein is transformed into stearin with the observed more rapid increase of titer.

Ellis[31] effects a constant circulation and contact of the hydrogen gas in accordance with the method shown by Fig. 21. The tank A contains a body oil, O, the space above the oil being filled with hydrogen under any suitable pressure. The tank is heated by the jacket S. A pump, P, withdraws the hydrogen from the upper part of the tank and impels it through the pipe D, into the lower part of the tank. Catalyzer is added to the oil when the proper temperature is reached, and the constant bubbling of a stream of hydrogen through the oil causes intimate contact between the roasting elements. After the operation is

[30] U. S. patent No. 1,026,156, of May 14, 1912.

[31] U. S. patent No. 1,040,532, of Oct. 8, 1912.

completed, the porous plate, fastened to a movable stem in the upper part of the tank, may be depressed to fit into the bottom of the conical base so that when the oil is withdrawn a good portion of the catalyzer remains without exposure to the air and may be used with perhaps a small addition of fresh catalyzer for the treatment of a succeeding charge of oil.

In U. S. Patent No. 1,043,912, Ellis hydrogenates oil (Fig. 22) in the autoclave A. The pump P circulates hydrogen gas through the oil. The treated product is run into the deodorizer D, where it is treated with superheated steam under diminished atmospheric pressure until the oil is freed from noxious gases or vapors. While the deodorization of ordinary cottonseed oil, for example, requires a temperature from 200 to 300° C. and a vacuum of down to one or two inches mercury, the deodorization of the hydrogenated cottonseed oil does not necessarily require as high a temperature and the vacuum "pulled" may be considerably less.[32]

Contrary to the opinion entertained by many, it does not appear needful to agitate the catalyzer primarily for the purpose of contacting it with hydrogen. Once the catalyzer is wetted with the oil there can no longer be any actual contact with the gas. Hydrogen reaches the catalyzer seemingly only through solution in the oil. The forces of adhesion effectually seal the catalyzer surface from the gas, and no measure of agitation by ordinary mixing apparatus will dislodge the film of oil. Of course, agitation secures the rapid replacement of more saturated by less saturated portions of the oil, but this replacement, under certain conditions, may proceed just as rapidly, simply by diffusion.

CATALYZERS.

Catalyzers, those bodies which modify reaction velocity without stoichiometrical participation in the reaction, are destined to find another important industrial application in the hardening of oils.

The previous illustrations show the variety of methods proposed for mingling oil, hydrogen and catalyzer. Among these are several of excellent efficiency. But, after all, the virility, so to speak, of the process depends on the *catalyzer*. With a powerful catalyzer the hydrogenation of oils becomes a rapid, simple procedure; almost, it sometimes seems, independent of the nature of the hydrogenating apparatus.

Catalyzers recognized as useful for the purpose are nickel and palladium, although platinum, copper, iron and other metals have been used to some extent. Nickel oxide, as stated, has been employed by Bedford and Ipatiew. Wimmer recommends organic salts of nickel such as the formate, acetate or lactate.

As nickel is probably the most important of these catalyzers, in view of its efficiency and relatively low cost, it will be first considered.

The preparation of an effective nickel catalyzer requires considerable care. The oxide or hydrate of nickel is first obtained by ignition of nickel nitrate, or precipitation of nickel hydrate from say a nickel sulfate solution by the addition of an alkali. Obtained in this or in any other suitable manner, the next step is the reduction to metallic nickel. For this purpose the nickel is placed in a receptacle which may be heated controllably, and hydrogen gas is passed over the mass at a temperature ranging from 250 to 500° C. or so, until water is no longer evolved.

The most sensitive catalyzers are obtained by reduction at the lowest possible temperatures. Nickel begins to reduce below 220° C., but at 270° C. the reduction is not complete, even after long duration of exposure to hydrogen. A temperature of 300 to 325° C. gives fairly complete reduction and is a satisfactory working temperature. The lower the temperature at which the nickel is reduced, the more sensitive it is to various external influences, hence the preparation of this catalyzer should be conducted not only with respect to degree of activity, but also with respect to longevity.

Nickel is easily poisoned by chlorine and by sulfur in the sulfide form. We have had no unfavorable results from the use of hydrogen gas passed through a wash bottle containing concentrated sulfuric acid and then conveyed directly to the catalyzer and oil. Traces of the acid were entrained by the gas, but the catalyzer remained in active condition during about two weeks' usage under these conditions.

Copper is much less sensitive to poisons than nickel, but, on the other hand, it is much less active.

Catalyzer made from the oxide without supporting material, weight for weight, is hardly as efficient as when the active surface is increased by the use of a carrier. Hence we find many proposals for the production of catalyzers with a great diversity of carriers, ranging from pumice stone and kieselguhr to charcoal and sawdust.

After reduction of nickel, as above, it should be kept out of contact with air, as it is extremely pyrophoric, and quickly loses its efficiency on exposure to the air. Consequently, when treating oil with such a catalyzer, it is advisable to free the treating apparatus from air by flushing with hydrogen; also it is well to heat the oil and bubble hydrogen through it for a short time prior to the introduction of the catalyzer.

Several methods of producing catalyzers have been the subjects of the patents, as, for example, that to Crossfield,[33] in accordance with which kieselguhr, asbestos and the like is impregnated with a solution of nickel sulfate and the impregnated material treated with alkali hydrate to precipitate nickel hydrate on the porous material. The product is then well washed, dried and reduced. If kieselguhr is used, the powder should contain about 30 per cent of metallic nickel.

A similar procedure is the subject of a patent to Kayser.[34] In this case, however, the nickel sulfate or other nickel salt in concentrated solution may be

[32] See also U. S. patents Nos. 1,037,881, 1,038,545, and 1,047,013.

[33] English patent No. 30,282, of 1910.

used in an amount to saturate keiselguhr while leaving it in an apparently dry condition, when it is incorporated with a molecular proportion of powdered carbonate of soda and the mixture thrown into boiling water, dried and reduced.

Seeking to overcome the disadvantage of ready oxidation in the air possessed by normal catalytic nickel, Kayser[35] reduces the nickel oxide or equivalent material at a temperature of 500 to 600° C. and then passes through the reduced material a brisk current of carbonic acid until the escaping gas proves no longer inflammable. By this method it is claimed that a catalyzer is secured which will remain perfectly cool on exposure to the air and even may be exposed for days without losing any of its catalytic energy.

Wilbuschewitch[36] proposes to secure more rapid reduction of catalyzer by agitating it in the presence of hydrogen in a heated rotary drum. The temperature during the treatment is stated to be 500° C. Wilbuschewitch[37] has patented a process of regenerating spent catalysts of the nickel type involving extraction with benzine, treating with alkali solution, acidifying, treating with sodium carbonate solution and reducing.

As a catalyzer in this field palladium has received considerable study, for, in spite of high first cost, its pronounced effectiveness, together with its ability to effect hydrogenation at relatively low temperatures, makes it particularly attractive.

Many years ago, Fokin[38] stated he regarded palladium as the most powerful of all catalyzers, he having found that reduction takes place readily at 80 to 90° C., while with nickel, a temperature of 180 to 200° C. was necessary for practical hydrogenation. Fokin's experiments at that time were concerned with electrolytic reduction. By this means he reduced linseed, wood, castor and cod liver oil. He found that while *palladium*-black would reduce oleic acil completely to stearic acid, that *platinum*-black under the same conditions gave only 24 per cent of stearic acid.

Paal[39] worked with colloidal palladium preparations and hydrogenated castor, olive, fish oil and animal fats. He found that sesame oil, after hydrogenation, showed the Baudoin reaction only very faintly, while cottonseed oil no longer responded to the Becchi and Halphen reaction.[40] Skita has worked with palladium incorporated with a protective colloid.

Karl[41] has studied, with considerale care and in a quantitative way, the action of palladium supported on various bodies. He found that palladium precipitated on finely divided nickel or magnesium proved effective catalytically, while if precipitated on lead, aluminum, iron or zinc, little or no hydrogenation was effected, owing to the anti-catalytic action of these metals. While metallic zinc is anti-catalytic, zinc oxide and carbonate have no such effect. In these investigations Karl worked principally with fish, cotton and castor oil and oleic acid.

[35] U. S. patent No. 1,004,034, of Sept. 26, 1911.
[36] U. S. patent No. 1,001,279, of Aug. 22, 1911.
[37] U. S. patent No. 1,016,864.
[38] 1,022,347, of April 2, 1912.
[39] Chem. Ztg., [2] 758 (1906), [1] 321 (1907).
[40] Ber., 41, 2282.
[41] Paal recommends (U. S. patent No. 1,023,753, of April 16, 1912) platinum or palladium chloride admixed with a neutralizing agent such as sodium carbonate.
[41] Inaugural Dissertation, Erlangen (1911).

HYDROGEN.

One of the problems in the hydrogenation field is that of a cheap supply of pure hydrogen. The demand for hydrogen in various directions has increased of late, and undoubtedly this will lead to improvement in the manufacture of the gas.

The two methods now most favored in the hydrogenation of oils are the iron sponge steam process and the electrolytic method.

For very large plants the iron sponge steam process is preferred, but it is relatively complicated and scarcely to be recommended for plants calling for 1,000 cubic feet of hydrogen, or less, per hour.

Lane's process is based upon the passage of steam over reduced iron and involves the generation of water gas to reduce and heat the iron oxide employed. For each cubic foot of hydrogen produced, about three cubic feet of water gas are required. The water gas has to be freed from sulfur, as otherwise the hydrogen would take up sulfur from the iron sponge and poison the catalyzer. This requires the purification of three volumes of water gas, from which, as stated, a yield of only one volume of hydrogen is obtained.

The cost of hydrogen made in this manner is about one dollar per 1,000 cu. ft.

In the electrolysis of brine to make caustic soda and bleach, there exists a by-product of hydrogen sufficient in amount to treat an enormous quantity of oil. Today a good portion of this hydrogen is allowed to go to waste. Eventually it may be used, to some extent at least, for hydrogenation purposes.

Generators for the production of hydrogen and oxygen by the electrolysis of water are furnished by the International Oxygen Co. One type has an output of at least 130 cu. ft. of hydrogen and 65 cu. ft. of oxygen per day, giving about 7 cu. ft. of hydrogen per kilowatt hour. At 2 cts. a kilowatt the hydrogen costs about one-fourth of a cent per cubic foot, if one disregards the value of the evolved oxygen.

The electrolytic process is simple and clean and is to be recommended, especially for plants of moderate requirements.

We have for some time used hydrogen gas derived in this way, and find it suitable for hydrogenation purposes without resorting to any extensive purification.

Abroad, electrolytic cells capable of furnishing hydrogen at high pressure are obtainable, but are very costly.

Very promising methods for the production of hydrogen are: (1) The removal of carbon monoxide and hydrocarbons from water gas by liquefaction; (2) the decomposition of petroleum at high temperatures; and (3) the passage of water gas and steam at a temperature of 500° C. over lime containing an iron catalyst.

One of the difficulties met with in the handling of hydrogen has been the loss by leakage of the gas. Under pressure and at a temperature of 150 or 200° C., hydrogen is surprisingly penetrating. A treating tank having an oil capacity of about one ton was tested to 150 pounds air pressure and found to be tight, but when hydrogen was introduced at 60 pounds pressure the leakage was tremendous.

A stuffing box tested at 120 pounds steam pressure emulated a whistle with hydrogen at *one-half* the steam pressure. Autoclaves with welded seams are desirable for high pressure and high temperature work. Moving parts should be avoided as far as possible.

USES OF HYDROGENATED OILS.

The aiblity to prepare from ordinary *liquid* fatty oils a fatty body of almost any desired degree of consistency renders hydrogenation especially attractive in the production of edible fats and soap-making materials. These are, undoubtedly, two of the most important applications, although hydrogenated oils are likely to have rather wide use in the arts. In the manufacture of lubricants, for example, the hydrogenated fats may be used to advantage.

HYDROGENATED OILS IN THE SOAP INDUSTRY.

By hydrogenation, oils which formerly made soaps only of soft consistency now yield the more valuable hard soaps. This has led to a very rapid development of the art with respect to the production of soap-making fats. In particular, fish and whale oils have been made use of, because these oils may be completely deodorized by the addition of hydrogen.

According to a Japanese chemist, Tsujimoto, the odor of fish oil is due almost entirely to a fatty constituent and not to so-called impurities. This fatty constituent is clupanodonic acid having the formula $C_{18}H_{28}O_2$, which, therefore, by the addition of 8 hydrogen atoms, becomes stearic acid. When hydrogenated down to an iodine number of about 50, fish oil has the consistency of hard tallow and the odor of fish oil is wholly absent. Even the fishy taste is scarcely in evidence.

For soap-making this product is satisfactory, as it complies with the test for a deodorized fish oil suitable for soap-making in that the odor of the original oil is not apparent when ironing laundered goods on which such soaps are used. If, however, the hydrogenation is not carried on to a point where the iodine number is approximately 50 or less, there is some danger that the fishy odor will become apparent during the ironing operation.

Crossfield & Sons[42] have patented, in some countries, the use of hydrogenated oil in the manufacture of soaps. They claim the hardened or hydrogenated fats have the advantage that a weaker brine suffices to separate the soap from the glycerine; further, that the soap produced from such hydrogenated fats is exceedingly hard; as, for instance, soap made from hydrogenated cottonseed oil is stated to be about 12 times as hard as that made from untreated cottonseed oil. This, of course, enables the admixture of a larger proportion of rosin, which naturally would be looked upon as a decided advantage.

In contrast to this, a German writer[43] states that the hardened oils form soaps which are too hard to give good lathering properties.

Since soaps are made almost invariably of mixtures of fats, it is under the control of soap-makers to use such an amount of hydrogenated fat as would give the requisite degree of hardness without sensible diminution in lathering power; hence the foregoing criticism seems to be without great weight.

It suffices to state that hydrogenated fats for soap-making purposes are being made abroad by a number of firms and are giving good satisfaction in many instances. The Germania works at Emmerich, Germany, offers on the market three grades of hardened oil.

In this country satisfactory results are being obtained commercially in the manufacture and use of hydrogenated oils in soap-making. Several plants are operating or planning to operate on the large scale.

EDIBLE HYDROGENATED OILS.

Since the addition of less than 1 per cent of hydrogen suffices to convert cottonseed oil or other vegetable oils into a fatty body of the consistency of lard, it follows that manufacturers of ordinary lard compounds (that is to say, a mixture of 80 to 85 per cent of refined cottonseed oil and 15 to 20 per cent of oleo-stearine) have promptly turned their attention to the production of the compound by a "self-thickened" cottonseed oil.

The high cost of oleo-stearine makes the method an attractive one, and the hydrogenated product from cottonseed oil has the advantage, if properly made, of being very stable in character.

We believe, however, that for best results it is desirable to hydrogenate the entire body of oil to a fatty acid titer of 36 or 38, or whatever consistency may be required, rather than to take 20 per cent or so of the oil and harden it to a titer of 52 or thereabouts and incorporate with unhydrogenated oil.

It appears that the hydrogenation of the total body of the oil, by transforming the linoleic and linolenic compounds and the like, has a tendency to improve the oil as regards its edibility, and certainly gives it greater stability.

EDIBILITY OF HYDROGENATED OILS.

It seems to be generally accepted by those who have investigated the matter carefully that the hydrogenated oils have as desirable a degree of edibility as the oils from which they are derived. It is even claimed that by destroying traces of certain unsaturated bodies thought to be slightly toxic in nature hydrogenation renders the oil better adapted for human consumption.

A question of serious import has, however, arisen

[42] English patent No. 13,042, of 1907.

[43] Seifensieder Ztg., 39, 660.

in the use of nickel catalyzer. Aside from the fact that by careless filtration, traces of the suspended nickel may be present in the product, there is the more serious problem of the actual solution of nickel to form nickel soaps which cannot be easily removed.

According to Bömer,[11] nickel is dissolved by oils during the hydrogenation treatment only when the oil contains free fatty acid in considerable amounts. A sample of hydrogenated sesame oil containing 2½ per cent of fatty acid was found to contain 0.01 per cent ash with 0.006 per cent nickel oxide. Whale oil, containing 0.6 per cent fatty acid, yielded 0.006 per cent ash and 0.0045 per cent nickel oxide. Such an amount of nickel presumably would not be tolerated in a product intended for edible purposes.

The Bureau of Animal Industry of the Department of Agriculture is now investigating the matter, and apparently intends to determine the relative degree of toxicity of the traces of nickel in the form existing in improperly made hydrogenated oil. We may add that, so far as can be ascertained, the department looks kindly upon the advent of hydrogenated oil in view of the likelihood that it is destined to prove a very acceptable substitute for higher priced animal fats and does not propose, according to my understanding, to venture any ruling until the matter has had protracted scrutiny.

It is our belief that the use of nickel in the form of an oxide, or the use of nickel catalyzer containing more than traces of oxide, is undesirable from the point of view of solubility in oil. Nickel, in the metallic state, cannot combine with a fatty acid to produce a soap, except with the elimination of hydrogen, and in the presence of an atmosphere wholly of hydrogen, because of mass action, such reaction would not be likely to take place. On the other hand, nickel in the form of oxide would yield water on combining with fatty acid which would be yielded practically into a vacuum as regards the vapor pressure of water.

Hence it seems to the writer that in the manufacture of products intended for edible purposes, care should be taken to maintain conditions such that the catalyzer, if of the nickel type, is preserved almost wholly in the metallic state. Also it is desirable to not force the reaction too rapidly, with the consequent danger of breaking down the carboxyl group and setting free water which would react to produce fatty acid.

Finally, it may be stated, by partial saturation of glycerides we have the possibility of preparing from tri-olein the oleo-distearine or the dioleostearine. Dioleopalmitin would give either oleostearopalmitin or distearopalmitin. From tri-olein we may have the two isomeric oleo-distearines, α- and β-oleo-distearine as well as α- and β-dioleostearine. Which of these we may be able to produce controllably and which may prove best from the edible standpoint are problems for the future to solve.

[11] Chem. Rev. Fett.-Harz.-Ind., 221 (1912).

THE ALCOHOL REQUIREMENT OF THE PURE FOOD AND DRUG LAW AND THE ACCURACY OF ALCOHOL ASSAYS OF PHARMACEUTICAL PREPARATIONS.*

By C. H. BRIGGS.

Before the Pure Food and Drug Law went into effect it is doubtful if manufacturing pharmacists paid very much attention to the accurate determination of the alcohol in their preparations. They were in position to know how much alcohol went into each preparation, and whether this amount of alcohol could be actually recovered was a matter of little moment. However, on the advent of the Pure Food and Drug Law, it became necessary to state on the label the percentage of alcohol in every preparation, and the problem of determining this exactly began to assume serious proportions. It is doubtful if the framers of the Pure Food and Drug Law had any thought of requiring a statement of the alcohol content of ordinary galenicals such as are put out by the manufacturing pharmacist, but it is probable that their real intention was to require the alcohol content of those medicines sold diectly to the laity. In order to do this, it was necessary to include all pharmaceutical preparations containing alcohol.

The first interpretation of the law, that the maximum amount of alcohol could be stated on the label, was a very practical one, and did not cause any undue hardship to pharmaceutical manufacturers. It was only necessary to know the amount of alcohol which went into an elixir, or in case of a fluid extract the amount which was usually obtained, to be able to fix upon a maximum percentage for a label claim which would not only be safe from the manufacturer's standpoint, but would also not deviate excessively from the actual alcohol content.

The later belief, however, that the actual percentage of alcohol must be stated on the label, is a matter of grave concern to the manufacturing pharmacist. To meet this requirement two courses are open:

1. To assay every preparation for alcohol and stamp the actual content on the label.

2. To have the label printed with a standard content of alcohol for each preparation and to adjust each individual lot to the standard.

The first method requires the special stamping of every bottle and is expensive. It also shows variation in the alcoholic content in the individual lots of a preparation which is apt to cause distrust on the part of the pharmacist and require an undue amount of explanation on the part of the manufacturer. Anyone who has had anything to do with the manufacture of fluid extracts, for example, knows that it is impossible to make several lots of the same kind and have the

*From the Journal of Industrial and Engineering Chemistry.

finished fluids contain the same percentage of alcohol. Variations in the amount of moisture and extractive in the drug, and slight variations in conditions and amount of alcohol lost, all tend to cause considerable variation in the alcohol content of the resulting fluid extracts. Hence, in order to make a fluid extract contain a standard content of alcohol, it is necessary to assay it for alcohol and finally adjust it to the standard by the removal or addition of alcohol. It is also advisable to assay the fluid extract again after it has been adjusted, for the adjusting of a large lot of fluid extract to within 1 per cent of alcohol is not an easy matter, and considerable variations are liable to occur. With this fact in view, the question naturally arises, how accurately can pharmaceutical preparations be assayed for alcohol?

In making alcohol assays there are several sources of error:

1. In Measuring the Sample.—An error of 0.25 cc. on a 25 cc. sample means that a 90 per cent alcohol will test 89 per cent and a 50 per cent alcohol only 49.5 per cent. An error of 0.1 cc. in measuring the sample means that a 90 per cent alcohol will test 89.6 per cent and 50 per cent alcohol 49.8 per cent. Then there is another similar error in adjusting the distillate to the definite volume required for taking the specific gravity.

2. Loss of Alcohol on Distillation.—There seems to be a slight loss of alcohol on distillation, due perhaps to a slight absorption of alcohol around the stoppers or a slight retention of alcohol in the flask and residue. It is not possible to recover *all* the alcohol from a liquid of more than 50 per cent strength unless it is diluted with water and double the amount of distillate is collected. This multiplies the error in the specific gravity by two and so increases the error. We have tried adding sodium chloride to the alcohol solution in the flask before distilling, but it does not seem to affect the results.

3. Error in Taking Specific Gravity.—An error of 1 point in the fourth place, or say 0.9541 instead of 0.9540, means an error of about 0.2 per cent alcohol and an error of 2 points in the fourth place means an error of 0.4 per cent alcohol.

The Westphal balance is not sensitive to better than 1 point in the fourth place and it requires careful work to get it that closely. The pycnometer method is more accurate but requires a much longer time, which is a very important consideration where a large number of determinations have to be made.

4. Temperature of Solution When Taking Specific Gravity.—This may cause considerable error and this point must be watched very carefully.

5. Essential Oils.—Essential oils are used in most elixirs and in many compound fluids and tinctures. Small quantities of essential oils distil over with the alcohol and water and dissolve in the distillate. This may increase the specific gravity and lower the alcohol results. Several experiments were tried to see what effect the addition of 1 per cent of essential oil would have on the assay of 50 per cent alcohol. It was found that in a series of nine determinations the results were low from 0.9 per cent to 1.4 per cent alcohol.

The effect of drug extracts on alcohol assays was also determined. A quantity of the drug extract was placed in the distilling flask with the usual amount of an alcohol solution of known strength and the assay made in the usual way. The results were as follows:

	ALCOHOL.		
	Per cent.	Per cent.	Per cent.
Alcohol used	49.7	51.25	56.8
Found by distillation	49.0	50.66	56.14
With extract Cascara Sagrada	48.66	50.16	56.8
With extract Gentian	49.0	49.68	55.4
With extract Belladonna	48.82	50.00	55.51

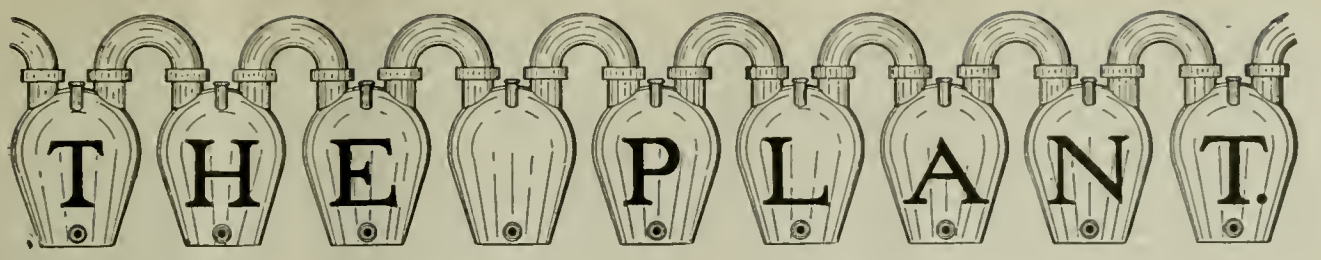
From this table it will be seen that while the results are about 0.65 per cent low without the drug extracts, that the average loss of alcohol is about 1 per cent when the drug extracts are present. Some of the alcohol is apparently held mechanically by the extractive matter.

The writer has had occasion to observe the results of 25 to 30 alcohol assays per day for three or four years, and while there is little doubt that one or a dozen alcohol assays can be made which will not vary more than 0.2 per cent or 0.3 per cent when great care is used, still in the regular assay of a great many samples much larger errors will creep in and results may be off as much as 1 per cent or 1.5 per cent alcohol. When we stop to consider that an error of 1 per cent in the alcohol assay of a single lot of 500 gallons of elixir means the addition of 5 gallons of alcohol, worth thirteen dollars, it is really a matter of considerable importance to the manufacturer.

The question now arises how closely will pharmaceutical preparations have to be adjusted to the label claim to be satisfactory under the Pure Food and Drug Law? This is a difficult question to answer. The rule in force in this laboratory is that all products must assay within 1 per cent of the alcohol standard on the label before they are accepted.

It is evident, however, that there are several large pharmaceutical manufacturers who are labeling their preparations with statements of the maximum content of alcohol, but it is an open question whether this will satisfy the requirements of the official board.

The writer believes that a ruling to the effect that fluid extracts and elixirs could be labeled with the maximum content of alcohol would be just and fair and would not in any way deflect the real intent of the Drug Law. It would certainly be a welcome measure to pharmaceutical manufacturers who are putting forth their best efforts to conform to the law.



ESTIMATING THE QUALITY OF PAPER.*

THE MICROSCOPICAL, PHYSICAL AND CHEMICAL TESTS OF THE UNITED STATES BUREAU OF STANDARDS.

It is a well recognized fact that an accurate knowledge as to the materials and chemicals entering into the composition of a paper is of great value to every paper maker who may be called upon to match a given sample. Manufacturers at present must depend on their personal judgment for such information, and the ability to correctly judge papers may only be required by long years of experience. To such an experienced man the first look at a particular sheet of paper reveals the general class to which it belongs, whether writing, printing, wrapping, board, etc. A second glance reveals the relative grade into which the particular class is subdivided. This preliminary information at once brings to the mind of the experienced man a picture of the general process of manufacture required to produce such a paper. By the use of his sense of smell he, in many cases, is able to determine whether it is animal sized or not; he presses his tongue against the sheet and says whether it is "water-leaf" or "sized" paper, and whether "slack," "medium" or "hard" sized; if a coated paper his tongue will indicate it. Upon closer inspection and a liberal use of the sense of "sight" and "touch," he is able to estimate the weight per ream, the thickness of the sheet, the fiber composition and general method of treatment in the beater room, on the machine and in the finishing room. He may also be able to give an estimate of bursting strength and general folding quality. The result of this method of testing is only comparative and, therefore, lacks fundamental necessity of numerical expression for record purposes.

At the present time there is developing, both within and without the paper trade, a growing interest in the subject of paper testing. There is a demand on the part of the buyer for better methods to enable him to determine the quality of a paper. That there is this growing interest in the subject and a general demand for standard methods of testing is most conclusively shown by the work which is being accomplished in the commercial paper testing laboratories that are starting up in various parts of the country.

This increasing general interest in paper testing has been the cause of developing a series of tests that apply both to the physical and chemical properties of a paper. These tests are not meant to give absolute values, but if due care is exercised in the selection of a representative sample and in making the necessary tests, then numerical values will be obtained which to a large degree indicate something of the quality of a paper. Such a method offers the only means whereby a record of a paper may be kept.

In this discussion of paper testing, it should be distinctly understood that these tests do not cover every quality of property a paper may have. The degree with which one sample is a color match for a second sample must depend upon the ability of the eye of the individual. The matter of "finish" is a second property, which so far cannot be expressed numerically, and for which there are no physical tests. The degree with which one sample conforms to another in finish is purely a personal element, and depends upon the experience of the individual.

At the present time there are no physical methods by which an accurate comparison may be made to determine when a paper contains a larger amount of dirt than is acceptable, or just what degree of "wild formation" shall render a paper nonacceptable. These two properties of "dirt" and "formation" are left to the judgment of the individual, and depend on a hazy mental idea of what he individually believes to be a point beyond which a paper becomes undesirable for the particular purposes for which it was intended.

The laboratory testing of a sheet of paper then narrows itself down to determining those properties which have a nearly fixed value, or may be expressed in definite numerical terms. These values are such that when due care is exercised two or more individuals using the same methods and samples and working independently will obtain duplicate results. In other words, such methods very largely eliminate the personal element of the individual wherever the properties of a paper may be given a numerical value.

The general examination of paper may be subdivided into three parts as follows:

Microscopical examination.

Physical tests.

Chemical analysis.

A microscopical examination will disclose the kind or kinds of fibers from which a given paper was made, and the experienced man will with considerable accuracy be enabled to estimate the proportions of various

*Paper read at a meeting held under the auspices of the Bureau of Standards at Washington, D. C., Jan. 13, 1913.

kinds of fibers used. The miscroscope also helps to indicate how much a stock has been beaten.

The testing to determine the physical properties of a paper is divided into determining: weight per ream, thickness, bursting strength, tensile strength, folding endurance, expansion and absorption.

The chemical analysis will disclose the amount of ash retained and the amount and kind of size used. A chemical examination will also give much information in regard to colors used. All of this information is of the utmost importance in determining the quality of a paper.

The principal purpose of a microscopical examination is to determine what fiber or fibers were used in making a paper, and then to estimate the relative proportion of each on a basis of 100 per cent for the total fiber composition. Such an examination requires the following apparatus: beakers, test tubes, slides for microscope, two long pointed steel dissecting needles, bunsen burner and tripod stand (or other means of heating sample), one large bottle of a ½ per cent solution of caustic soda, one small bottle of 25 per cent hydrochloric acid, six small dark colored glass bottles, with dropping stoppers for stains, small pieces of filter paper and a miscroscope which for ordinary work should be capable of magnifying about forty-five times. The binocular microscope will be found to be best suited for estimating work where it is desired to study the markings and special characteristics of a fiber, then a microscope capable of magnifying from 150 to 200 times should be used.

As all vegetable fibers are highly transparent and almost entirely colorless, when seen under the microscope, it is very necessary to use some staining solution to color the fiber in order to bring out their size and shape and general markings. The best stain for this purpose is the so-called "Herzberg" stain, which is what is known as a selective stain, that is, it has the property of giving a yellow color to most uncooked fiber, such as mechanical wood; chemical woodpulps are colored in indigo blue; and cotton, linen and some other fibers are colored in wine red.

The staining solution is made up as follows:

SOLUTION "A."

Zinc chloride	Gm. 20
Water (preferably distilled)	Cc. 10

SOLUTION "B."

Potassium iodide	Gm 2.1
Iodine crystals	Gm. 0.1
Water (preferably distilled)	Cc. 5.0

Dissolve "A" by adding the water to the zinc chloride in a glass beaker.

Dissolve "B" by adding a few drops of the water to the potassium iodide and iodine crystals in a glass beaker and after dissolving add the remainder of the 5 Cc. of water.

The two solutions—"A" and "B"—are then mixed together and allowed to stand for twenty-four hours to settle, after which the clear liquid may be poured off and divided between two of the dark glass bottles with the dropping stoppers. All iodine solutions will fade in light, and should, therefore be kept in the dark as much as possible.

It is a very good plan to use two more of the dropper stoppered bottles to keep a concentrated solution of zinc chloride and water in one and a concentrated solution of potassium iodide and iodine in water in the second; these two solutions will be found handy in adjusting the Herzberg stain.

The preparation of a sample of paper for the microscope is as follows: Several small pieces of paper of about the area of a cent are cut from different parts of the sheet of paper; these pieces are then placed in a breaker and covered with ½ per cent caustic soda solution, the whole mass is then brought to boil over a suitable heating device. After boiling for about a minute, the liquid is poured off and some tap water added to wash out the caustic soda, and two or three drops of a 25 per cent hydrochloric acid solution added to neutralize the alkali.

The slightly acid solution is then poured off and enough of the small pieces of paper is pinched off and rolled into a ball of about the size of a pea. This small ball of pulp should be well rolled between the thumb and finger and then placed in a test tube and the test tube about half filled with water. Care must be exercised to rinse the hands after working each sample, to keep from contaminating the sample following. The test tube is then shaken vigorously until the paper has been entirely broken up and the fibers are well separated. A few fibers are next removed on the point of the microscope needle from the test tube, and a small sample is placed on each end of one of the microscope slides. The slide should be held in the holder over some black surface, as it is a great help to the eye to look at the white fibers against a black background. The wet fibers on a slide may best be dried by covering them with good filter paper and left for a few minutes to dry in the air.

The fibers are thoroughly dried and a drop of the Herzberg stain is added, and then the fibers are well "teased" out by the use of two microscope needles, a cover glass is placed upon the fibers and well pressed down, all the stain pressed out around the edges of the glass being removed with filter paper, and the slide polished with paper or cloth.

The slide is next placed under the microscope and after studying the various fields an estimate of the proportion of each of the various kinds of fibers may be given.

It is best to use four stains for this work, that is, each stain is of slightly different strength as each one gives the best results on certain fibers. For example, a stain that clearly brings out the wine red color on cotton and linen fabrics, as a rule, usually does not give the best blue color on bleached soda and sulphite pulp; the same stain on ground woodpulp has almost no effect at all.

In making up a stain to produce the best color on the particular fiber, the following points should be remembered:

Two or three drops of water added to a good stain for rag and bleached chemical wood will tend to fade out the wine red color, the blue color will remain nearly unchanged, and the yellow color on ground wood will be brought out very much clearer. In other words, a good rag stain, when used on ground wood, produces almost no coloring of the ground wood fibers.

The addition of two or three drops from the bottle containing the concentrated solution of iodine and potassium iodide, in water, will produce a deeper wine red or rag fibers, while the addition of a few drops of concentrated solution of zinc chloride in water will produce a deeper blue on chemical wood fibers.

It should be remembered that these iodine solutions will continually fade out, and that the best results may only be obtained when the stains give the proper colors.

The easiest and best way in which to secure a stain of the right coloring capacity is to keep on hand the following pulps: Bleached soda and sulphite pulps, unbleached sulphite, ground wood, and beaten rag stock. The rag stock may most easily be secured by using a sheet of good quality of filter paper, which is always made from "all rag" stock. Now take small bits of the bleached soda and bleached sulphite pulp and thoroughly mix them, after first separating them in water in a test tube. Place a small sample on a microscope slide, thoroughly dry the fibers, add one drop of stain, separate fibers with the needles, place cover glass in position and place slide under microscope. Each fiber seen should be of a blue color, the sulphite fibers appearing much wider and longer than soda fibers and should show a lighter blue color, as the fiber is more translucent than a soda fiber, while the soda fiber should take a darker blue color.

Soda and sulphite fibers should show a slight color difference, and soda fibers being colored a darker indigo blue, while sulphite fibers should be colored a lighter indigo blue. If this color difference is not clearly brought out then either water or zinc chloride solution should be added, depending on whether it is desired to weaken or deepen the colors.

Some rag fibers should now be added to the test tube, and a second slide made up, using a bottle of stain which is intended to produce best results on mixture of rag and woodpulps. This second stain is adjusted by adding water, zinc chloride, or iodine-potassium-iodide, or all as may be needed until the three fibers, soda, sulphite and rag, are all clearly brought out.

A third stain should be prepared for such papers as may contain ground wood by using mixture of ground wood and unbleached sulphite, and then adjusting the stains to give the best colors. The proper yellow for ground wood is the lemon yellow, never an orange yellow, as then the sulphite pulp is too slightly colored and ground wood estimates are necessarily too high.

The experienced man may by using this method get some very surprising results. The Bureau of Standards believes that in papers containing mixtures of rag and bleached chemical wood, a careful miscroscopical estimate is well within 5 per cent of the correct fiber contents. For papers containing ground wood, especially where the percentage of ground wood is high, then the degree of accuracy is within 10 per cent of the correct fiber contents.

For laboratory use, the quickest sheet weighing device is the quadrant paper scales, so graduated that the corresponding ream weight—either 500 or 480 sheets—is read off directly in pounds.

Thickness of a paper may best be determined by the use of a spring micrometer having a hand that travels around a circular dial. This dial is graduated into thousandths of an inch and may be read to ten thousandths. In using such a gauge care should be taken to see that the pressure on the paper is constant, and also that the pressure surfaces are large enough not to compress the paper.

The bursting strength of a paper is determined with a machine by which the paper is firmly clamped against a rubber diaphragm, through which the pressure is applied to a circular area of the paper measuring one square inch. The actual pressure of the liquid under the rubber diaphragm required to burst the paper is registered on a carefully calibrated pressure gauge, reading pounds per square inch. An average of ten readings is taken as the correct bursting strength.

The tensile strength of a paper is determined upon a suitable machine, capable of accurately recording the tension required to break a strip of paper, when held at each end by suitable clamps, and the clamps are moved apart until breaking of the paper occurs.

The folding endurance is measured on a machine in which a strip of paper of definite size is clamped. The clamps are held apart under definite tension and the paper is caused to bend back and forth upon itself until the fibers wear through at line of folding. The number of double folds is recorded automatically by a suitable device.

Expansion of a paper may be determined by submitting the paper to different atmospheric conditions and noting resultant size of sheet at each change in the atmosphere.

The measure of absorption of a paper is the height to which, in a given time, a liquid will rise by capillary action, when one end of a vertically held strip of paper is immersed in water. This test, as well as all physical tests, must be made under a uniform condition of humidity.

The work of the paper laboratory at the Bureau of Standards comprises the testing of papers for the government service and the general public; also a study of methods of paper manufacture for the purpose of obtaining information of value in the preparation of government paper specifications. Information thus obtained is also at the disposal of the general public, who may be interested in selling or buying paper under definite requirements.

It is not the intention of this bureau to go into general commercial paper testing, for the reason that there are regular commercial laboratories that are well equipped to do this work. Tests in dispute between outside parties will be taken up as an absolutely disinterested referee; in such case the bureau will very willingly give all possible assistance.

The equipment of the paper laboratory is at the service of the paper manufacturer as well as the user of paper for the investigation of problems of wide general interest, and it is desired to impress upon the trade and the general public that they are always welcome to such information as we may possess, provided such information does not come to us in a confidential manner.

The United States government throughout its various branches consumes 40,000,000 lbs. of paper each year. This large amount of paper includes almost every grade or kind on the American market. The acceptance or rejection of such a large and varied amount of paper necessarily involves good judgment on the part of the paper inspector, together with an intimate knowledge of the manufacture of all kinds of paper, and a knowledge of the various uses to which each grade may be put. Is it reasonable to expect to find one or even two men who combine such a knowledge?

It is the firm belief of the Bureau of Standards that all manufacturers and users of paper will readily recognize that a correct set of definite chemical and physical tests, when carried out under uniform conditions will give more reliable results than could be obtained in any other way. It is also the belief of the Bureau of Standards that a knowledge as to the nature of our methods of paper testing, as well as the manner in which a paper specification is developed, will tend to convince the trade of the fairness with which this work is carried on.

The value of coffee importations in the calendar year 1912 amounted to 130½ million dollars, against 97 million in 1911, and 74 million in 1910, 87 million in both 1909 and 1904, and 109 million in 1892, the former high-record year. The quantity, however, imported in 1912 is materially less than in 1909 or 1904, the number of pounds imported in 1912 being 943 million, against 1,140 million in 1909 and 1,113 million in 1904.

Among the many progressive measures taken to maintain the supremacy of Lyon in the silk industries of Europe, the latest is the creation of a chair of sericulture in the scientific department of the University of Lyon. Due to the foresight and liberality of the Chamber of Commerce of Lyon, the necessary funds have just been voted for salaries for a professor and an assistant to conduct the new course, which will be a part of the general instruction in applied zoology.

PULP AND PAPER FROM WASTE RESINOUS WOOD.

The Bureau of Chemistry of the U. S. Department of Agriculture has recently issued a report giving the results of a study on the making of pulp, paper, turpentine, rosin oil and methyl alcohol from waste resinous wood. The investigation was made in the Leather and Paper Laboratory of the Bureau by E. P. Veitch and J. L. Merrill. The report was published as Bulletin No. 159, and the following matter is taken from it:

The results of a study on the making of pulp, paper, turpentine, rosin oil and methyl alcohol from waste resinous wood, made in the Leather and Paper Laboratory of the Bureau of Chemistry of the United States Department of Agriculture by E. P. Veitch and J. L. Merrill, are interestingly set forth in a report published as Bulletin No. 159 of the Bureau of Chemistry. It is believed that the simultaneous production of these articles from resinous wood is one of the most promising lines of industrial development which, up to the present time, has remained practically untouched, and that the upbuilding of chemical industries in the south and northwest, close to the raw materials, will be of great benefit to the agricultural interests of these regions.

The idea that the waste long leaf yellow pine, Norway pine, Douglas fir and other woods rich in resins can be used for the making of paper, wood, turpentine, rosin oils and similar products is not new, but the industry is just beginning to develop. It has received, the report says, more or less attention in this bureau during the past seven years, where information as to its feasibility and practicability and as to the yields and character of the products which may be made, has been gathered. This information points the way to the means whereby valuable timber may be conserved and the menacing waste wood of the lumbering operations may be profitably utilized.

The making of paper from these woods presents no unusual difficulties; in fact, several mills are running almost exclusively on such woods, while others use them in greater or less quantity. The recovery of wood turpentine, pine oils and other products from resinous woods by steam or destructive distillation has been fairly well worked out, and, when a plant is properly located and equipped and operated skillfully, this industry is proving profitable.

The production of rosin oils, tars and pitches from common rosin is also a thoroughly established, well understood and profitable industry.

With these successful results in view, it is at once clear that a combination of the three industries, using waste wood as the raw material from which all the products of these industries may be made, should be more profitable and require less capital, equipment and labor than the three when conducted separately. Since each of these industries, paper making, wood dis-

tillation and rosin oil production, is already well developed and the details quite well understood, no experimental demonstration on a manufacturing scale is needed to prove the practicability of the combination of the three. In short, such combination under one management is the most logical industrial condition.

The experiments to be described were conducted with what is known in the south as "lightwood," which is a long leaf yellow pine that has lain in the forest until practically all the sap wood has decayed, leaving the heart wood sound. Such wood is rough, full of knots and the greater part of it more or less charred from forest fires. For the experiments both the freshly prepared and the steam-extracted chips obtained from a steam wood turpentine plant were carefully selected to represent the average wood received at the plant.

The percentage of rosin which the chips contained was determined by extracting with ether and drying the extract in the water oven. The fresh chips contained 18.5 per cent of rosin on the basis of the water-free wood, while the chips which had been steamed at the turpentine plant contained 19.3 per cent. The total oil recovered from the black liquor was approximately 2 to 4 per cent lower than these figures.

The results are applicable only to average lightwood. Yields will naturally vary with the kind of wood employed. A cord of slabs and lap will yield less turpentine, rosin or rosin oils than a cord of lightwood, while freshly split old stumps will yield more; old slabs and lap yield less than the fresh or green. In other words, the yields differ in quantity, but not in kind with the character of the wood employed. The wood of long leaf pine saw timber contains, as a rule, from 2 to 6 per cent of resin and about 0.2 to 0.5 per cent of turpentine, and the short leaf pine saw timber about the same. It would probably not be profitable to attempt to recover rosin oils and by-products from wood containing as little as 2 per cent of resin. The value of the by-products from such wood will rarely reach $3 per cord, and even in well designed and efficient works it is doubtful if a profit can be secured from them.

The experimental cooking was done in a small rotary digester holding about 4 kilograms (8.8 lbs.); from 2 to 4 kilograms of air-dry wood were cooked at a charge. Wood and dilute alkali were placed in the digester, which was then rotated to insure perfect contact and heated during rotations until the pressure reached 40 to 50 lbs., when the digester was connected with a condenser and water and turpentine distilled at a stated pressure. The digester was then closed and again rotated for from 15 to 20 minutes at 40 to 50 lbs. pressure and again relieved as before, this procedure being repeated four or five times. The condensed water and turpentine were received in a graduated constant level vessel in which the turpentine could be accurately measured after separating from the water. The volume of water condensed was also noted. After the turpentine had ceased to distill in measurable quantities the wood was cooked at different temperatures for various periods of time. The chips as received from the chipper were very irregular in size and shape, varying from coarse dust to pieces an inch thick and several inches long. They were screened into three sizes—those smaller than ¼-in. mesh, 31 per cent; those ¼ to 1 in. mesh, 44 per cent, and those larger than 1-in. mesh, 25 per cent of the wood. This separation was made in order to obtain data on the quantity of the various products that could be obtained from each of the several sizes and the time required to steam off the turpentine and to cook properly the chips of different sizes.

When fresh chips were used approximately 86 per cent of the total crude oils recovered were obtained in the first 30 minutes' relieving from the chips passing a ¼-in. mesh; 82 per cent from the chips passing between a ¼ and ½-in. mesh; while but 71 per cent were recovered from the chips larger than 1 in. The recovery in subsequent relievings falls off rapidly from the fine chips, more slowly from the medium chips and still more slowly from the coarse chips. Not all the turpentine was removed from the coarse chips. The total quantity of crude oils recovered was least from the coarse and greatest from the medium chips. There is no doubt, however, that the quantity of crude oils in the chips was least in the fine and greatest in the coarse, since the oils volatilize readily from the fine chips on exposure and very slowly from the coarse chips.

The quantity of crude oils actually recovered from the chipped lightwood under very favorable laboratory conditions was at the rate of from 10 to 13.2 gallons per 4,000 lbs. of wood containing 20 per cent of moisture, this percentage being an assumed quantity, approximately the average percentage of moisture in air-dry, seasoned wood. This yield is considerably below the yield generally claimed by steam wood turpentine producers, but agrees quite closely with the experimental work of the laboratory at steam plants and also with the census reports.

Data of the same general nature were obtained in the distillation of the steamed chips. A smaller percentage of the total oils recovered was obtained in the first relieving, but this percentage was greatest from the fine chips and least from the coarse. The recovery decreased more rapidly from the fine and medium than from the coarse chips. These figures also indicate the quantity of crude oils left in 4,000 lbs. of each size of chips steamed in stationary retorts. This quantity is from 1 to 2 gallons in fine, 3¾ to 3¾ gallons in medium and practically 4 gallons in coarse chips. In other words, from 2 to 3.3 gallons of crude oils per cord remain in ordinary lightwood chips, steamed in the usual way in upright retorts.

It will be observed that there is some variation in the total time of relieving and in the volume of water distilled among these experiments. Close observation of the accumulations of the oils indicates that these variations were not sufficient to cause a material difference in the amounts of oil recovered.

In the experiments with fresh chips in the first relieving or the first stage of the distillation, it required approximately 14 parts of water to remove 1 part of oil from the fine chips, 13 parts to remove 1 part from the medium chips and 30 parts to remove 1 part from the coarse chips. The proportion of oils to condensed water decreased very rapidly, and in the fourth or next to the last stage it required approximately 500 parts of water to remove 1 part of turpentine from the fine chips, approximately 350 parts to remove 1 part from the medium, and approximately 900 parts to remove 1 part from the coarse chips. Considering the whole distillation (four relievings), 1 part of oils was removed from the fine chips by approximately 51 parts of water, from the medium by 47 parts and from the coarse by 90 parts. From the steamed chips 55 to 200 parts of water on the fine, 90 on the medium and 125 on the coarse were required to remove 1 part of turpentine in the first stage, and from 500 to 1,000 parts were required in the final stage by chips of all sizes. Of the total oils recovered, 1 part required from 133 to 310 parts of water, the greatest proportion being required by the coarse chips.

From chips which would pass an inch screen more than 90 per cent of the recovered turpentine was removed in two relievings and that the total time of steaming to accomplish this was from 1 to 1¼ hours.

In these experiments the purpose was to remove all wood turpentine and pine oil from the chips and not to determine the best conditions for doing this. Steaming was continued until the proportion of turpentine to condensed steam or water was much smaller than is usual or would be profitable on a commercial scale. Apparently all light oils, turpentine and pine oils, which could be obtained under the conditions, were removed.

It has been observed by the Bureau of Chemistry in refining crude wood turpentine with saturated steam that the lighter oils, those that may properly be termed "wood turpentine," distill at the rate of approximately 1 part of turpentine to 1 part of water, but this proportion slowly changes throughout the distillation, and toward the close, and when the heavy oils or pine oils only are distilling, there is only 1 part of turpentine to 5 or more parts of water. For the distillation of practically the whole of any volume of ordinary crude wood turpentine the distillation of from three to four times as much water is necessary. At the best 10 to 15 parts of water to 1 part of turpentine were required in these experiments, and the same proportions have been observed at steam turpentine works.

In the distillation of crude turpentine from wood with steam, it is desirable for economic working to approach these proportions as closely as possible, though it is almost certain that they can not be equaled and absolutely certain that they can not be materially increased. Every effort should be made to have the steam carry as large a proportion of turpentine as is practicable. It is evident that if the proportion obtaining in refining can be had in steaming from the wood, steam consumption can be greatly reduced and the cost of equipping the plant and of making turpentine considerably lowered. Experiments are being conducted with this object in view. The experience and observations of the Bureau of Chemistry indicate that this condition can best be secured by relieving periodically from the retort. After the removal of the easily freed oils, which are very largely obtained in the first half hour of steaming without pressure, the valve in the outlet pipe to the condenser may be closed and the chips subjected to 40 to 50 lbs. of steam pressure for from 20 to 30 minutes, when the outlet valve may be opened for an equal period, maintaining the pressure all the time. This steaming and relieving may be alternated until it is no longer profitable to steam the chips.

PULP-COOKING DATA.

An additional quantity of water was placed in the digester with the chips and the alkali solution to distill off all the turpentine. Thus, during the early stages of the cooking, while the turpentine was being steamed off, the cooking of the fiber was conducted at low pressure with a dilute alkali solution. The concentration of the alkali solution increased gradually through the distillation of water and turpentine, until for the final stage the cooking was conducted in a 20 to 27 per cent alkali solution. During the steaming period, the pressure never exceeded 50 lbs., while the digester was closed and did not fall below 25 to 35 lbs. during relieving.

All of the cooking data so far as they relate directly to the production of pulp have been brought together in tables (which are omitted here).

The wood as received, approximately 30 per cent of which would pass a ¼-in. screen and 25 per cent which would not pass an inch screen, could of course not be cooked to produce a uniform pulp. The fine material was overcooked and weak, while the large pieces were cooked only superficially, often remaining hard in the centers. These facts are shown by the results of cooks 1 to 3.

The cooking data show a low consumption of alkali and a high yield of fiber. This is due partly to the fact that the cook was made for the production of a strong wrapping paper, for which the wood employed was suitable only, because of the charcoal which is almost invariably present in lightwood. The pulp

after milling was very firm and strong and the fiber long and well separated in every way suitable for making strong wrapping papers. The average air-dry unbleached pulp approximated 45 to 50 per cent from wood which contained about 18 per cent of rosin. The total time of cooking was somewhat under the usual time required for cooking wood by the soda process. Probably the time required in the mill to steam off turpentine and to cook for a strong wrapping paper is slightly longer than that required in these small-scale experiments. This time will naturally differ considerably with mill conditions. In no case do the results indicate more than a normal loss of fiber through the action of the alkali. It is true that the yields of fiber from the finest material were lower than those from larger chips, though not differing greatly from the yields from chips larger that ¼ and smaller than 1 in. As previously stated, however, the pulp from the finer chips was quite weak and overcooked.

It has been established in paper mills and on a commercial scale that a very good grade of wrapping paper is made from long leaf pine. Samples have been tested in the Bureau of Chemistry which show a strength factor of from 0.7 to 1. This is practically equal to similar paper made by chemical processes from spruce.

TREATMENT OF THE BLACK LIQUOR.

The black liquor and washings from the cooks were evaporated at atmospheric pressure, dried in vacuum and weighed. The residue was then destructively distilled in round, hard glass flasks.

The oils produced in distilling the dry black liquor were shaken several times with a 9 per cent caustic soda solution until no more was dissolved, for the purpose of separating creosote and other alkali soluble oils, the alkali solution containing these being subsequently acidified to insure separation of the oils. The oils insoluble in alkali were then fractionally distilled from an ordinary still; that distilling below 250° C. was classed as rosin spirit, as is the commercial practice, and that distilling from 250° to 400° C. after the more or less complete separation of a crystalline body, retene, was classed as rosin oil. Retene was present in all the fractions distilling at from 355° to 400° C., the largest quantity distilling between 388° and 393° C., or at the boiling point of retene, 390° C. The retene was separated as far as practicable from the rosin oils by chilling and cold pressing, but it is relatively certain that this procedure did not completely separate it from the oils, which in consequence contained some of it dissolved in them.

The quantities of the several constituents separated from the crude oils which were obtained by distilling the black liquor show some rather decided variations when calculated on the basis of the dry liquor. Thus the phenoloid bodies vary from 16.9 to 23.1 per cent, light oils from 11 to 15.9 per cent, retene from 2.7 to 11.2 per cent and rosin oils from 58.8 to 63.9 per cent. The cause of these variations is not definitely known, but it is believed that it lies in variations in the speed of distillation, variations in atmospheric pressure on different days and in unavoidable errors of measurement, errors accentuated by the comparatively small volumes of products obtained.

From these data the approximate percentage of each of the constituents of the crude oil obtained from this particular lot of wood may be thus stated:

	Per cent.
Phenoloids	18
Light or rosin spirits	11
Retene	5
Heavy or rosin oils containing an unknown quantity of retene	61

There is no question as to the profitable utilization of at least two of these—the light oils or rosin spirits and the heavy or rosin oils. Both of these products find a ready market, the former as a paint and varnish vehicle and the latter in the preparation of printers' inks and greases of various kinds. For the latter purpose it would appear unnecessary to separate the retene, as it is quite unctuous and would assist in giving body to the grease. Wood creosote may be separated from the phenoloids or alkali soluble oils which also serve in the preparation of antiseptic solutions or washes.

When the several constituents are figured on the basis of the dry wood, it is found that by the procedure outlined the wood yielded approximately the following results:

	Per cent.
Phenoloids	3
Light oils (below 250° C.)	2
Heavy oils (above 250° C.)	10
Retene	0.6

OTHER EXPERIMENTS WITH THE BLACK LIQUOR.

The black liquor was treated in several other ways. It was saturated at room temperature with carbon dioxide; then, under a pressure of 19 pounds, heated to 100 C., cooled and filtered. Filtration was slow when the mass became cold. The filtrate from the carbon dioxide precipitate gave a precipitate with hydrochloric acid. In a black liquor which contained 11.1 per cent of organic matter in solution, carbon dioxide precipitated 4.9 per cent and acetic acid precipitated 1.2 per cent from the filtrate. The carbon dioxide precipitate was dried and dry distilled. It yielded approximately 51 per cent of distillate, 17 per cent of water, 12 per cent of heavy oils, 11 per cent of light oils, and 6 per cent of creosote oils. The acetic acid precipitate did not contain all of the rosin removed from the wood by the alkali.

SUPPLY OF WASTE RESINOUS WOODS.

The supply of waste resinous wood suitable for the manufacture of paper, turpentine, rosin, rosin oils, methyl alcohol, etc., can be only approximately estimated. The census figures for the lumber cut in 1910

are: Long leaf pine, approximately 14,000,000,000 board feet; Douglas fir, 5,000,000,000 board feet; western pine, over 1,000,000,000 board feet; or a total of approximately 20,000,000,000 board feet. Authorities agree that at least 60 per cent of the tree as it stands in the forest is wasted in converting it into lumber, and that 25 per cent of the trees remain in the forests to rot or be destroyed in forest fires. That is, approximately 5,000,000 cords of waste wood are left annually in the forests in the lumbering of resinous woods, leaving out of consideration the dead and fallen timber in the uncut forest. This waste has been going on for many years. The sap or nonresinous part of the wood rots away in a few years, leaving the heart, or resinous portion, which will last indefinitely. Probably half of this annual forest waste becomes "lightwood," such as is used in the production of wood turpentine and tar. This material has been accumulating for years, and will probably continue to be added to for many more years.

In addition to this waste there is also a large source of supply in the stumps of cut-over lands and in the slabs and edging usually wasted at the mills. Altogether there are fully 8,000,000 cords of waste resinous woods annually produced in the lumber industry. This waste wood would yield all the wrapping, building and other low grade colored papers, and all the rosin, rosin oils, turpentines, rosin spirits and methyl alcohol which are now being produced in this country.

COST OF WASTE RESINOUS WOODS.

The cost of waste wood delivered at the mills in the South varies widely, but rarely exceeds $5 a cord. The Bureau of Chemistry has found that the average cost of lightwood delivered at the turpentine plants approximates $3.50 a cord. In case the wood is gathered by a lumbering company from its own forests and over its own tramroads this cost frequently does not exceed $2.50, and may fall as low as $1 a cord.

The stumps of long-leaf Norway pine and of Douglas fir, after the timber has been cut several years, are usually much richer in resins than average lightwood. They are, therefore, especially suitable for the production of wood turpentine, rosin and rosin oils. If care is taken to free them from earth, they are suitable for making paper. The cost of stump wood is often decidedly higher, especially in the West, than that of lightwood, because of the difficulty of removing stumps from the ground. This is best done by blasting, which has been found to cost approximately 5 cents a stump for long leaf pine of an average diameter of 13.6 inches. Approximately 45 such stumps, 2½ feet tall, will yield a cord of wood, which makes the cost on the land approximately $2.25 a cord, which should be added to the cost of lightwood delivered at the mill, to give the approximate cost of stumps at the mill. The average cost of removing Douglas fir stumps varying from 1 to 4 feet in diameter is about 84 cents each in Washington state, and 9 such stumps, averaging 3 feet in length and 2 feet in diameter, will yield a cord of wood. This makes the cost of the wood piled on the land ready to ship approximately $8 a cord, or possibly $10 a cord at the mill.

In estimating the cost of removing and gathering stumps the increased value of the land for agricultural purposes must be considered. The value of the land will, in many instances, especially in the South, be increased sufficiently to pay for the cost of removing the stumps, and in other cases this increased valuation will greatly reduce the cost of the wood at the mill.

Papermakers will undoubtedly question the practicability of using stumps for making paper because of the earth adhering to them. This can be largely if not entirely removed by proper methods; and as material worth even less than wood a ton is profitably purified it appears reasonable to suggest that sump wood can also be profitably cleaned for papermaking, at least in those regions far removed from the papermaking centers.

CONCLUSIONS.

It has been fully demonstrated, both in the laboratory and in the mill, that paper of good quality can be made from pine wood. The Bureau of Chemistry has called attention to this fact and to the industrial opportunities in this field in two former publications.

It is feasible to combine three well developed chemical industries—papermaking, wood distillation (in a modified form), and the manufacture of rosin oils—and thus to obtain from a single raw material, waste resinous wood, practically all the valuable constituents which it contains. The country's sources of paper, turpentine, rosin oils and wood alcohol can be greatly augmented and the injury to forests by fire and insects materially reduced by the utilization of this wood. It is believed that the results here presented will hold, approximately, for good average lightwood, except as to refined wood turpentine, which should run higher than here found. Especially is this true of the long leaf lightwood of North Carolina, which, experience has shown, yields more wood turpentine than does the lightwood of Florida. This fact is possibly due in part to climatic conditions, the longer and hotter summer of the South volatilizing more of the light oils.

The approximate yield for 4,000 pounds of cord wood air dry (3,200 pounds of moisture-free wood) of the valuable products and the value of each, together with the total value produced from a cord, is shown in the following table. The values are approximate wholesale values at the plant.

Refined wood turpentine, 6 gallons, at $0.40	$ 2.40
Pine oils, 7 gallons, at $0.35	2.45
Rosin spirits, 11 gallons, at $0.20	2.20
Rosin oils, 40 gallons, at $0.35	14.00
Phenoloids, 12 gallons, at $0.06	.72
Crude methyl alcohol, 3.5 gallons, at $0.35	1.20
Unbleached pulp, 1,440 pounds, at $0.0175	25.20
Total	$48.17

Thus products worth $48.17 are made from wood which costs from $2 to $4 delivered at the works.

MANUFACTURE AND USES OF CYANAMID.*

By E. J. PRANKE.

The problem of the fixation of atmospheric nitrogen is one which has engaged the attention of scientists for the greater part of a century. The rapid growth of the fertilizer industry that has attended the development of agricultural science, and the great increase in the number and extent of chemical industries, during the past fifty years, has emphasized the necessity for artificial methods of maintaining and increasing the world's stock of combined nitrogen. One of the influences that stimulated immediate action was the introduction in 1887 by MacArthur and Forest, and at about the same time independently by Siemens and Halske, of Berlin, of the Cyanide Process for leaching gold and silver from their ores. This produced a strong demand for cyanides, which had hitherto been used to the extent of only a few hundred tons a year, principally in the dye industry and to a smaller extent in electroplating.

Attempts had been made early in the nineteenth century to bring about the direct synthesis of cyanogen from atmospheric nitrogen and carbon. Among other processes, that worked out in 1847 by Bunsen and Playfair, in which barium carbonate was heated in an atmosphere of pure nitrogen, seemed promising, but did not prove to be commercially successful. The introduction of the electric furnace in 1894 by Moissan and by Willson, for the production of carbides on a large scale, gave new direction to the researches. Siemens & Halske, among others, adopted it for the working out of the problem of nitrogen fixation. In 1895 they worked on the process of Prof. H. Mehner, which consisted in fusing a mixture of sodium carbonate and carbon and conducting nitrogen through the hot mass. In the same year they took up the process of Prof. Adolph Frank and Dr. Nicodem Caro, which consisted in subjecting a mixture of barium carbide, sodium hydroxide, potassium hydroxide and carbon at a high temperature to the action of steam and nitrogen. Frank and Caro, with the co-operation of F. Rothe, soon learned that dry nitrogen is essential to successful absorption. In 1898 it was found that barium carbide alone, heated to a temperature of 700 to 800° Centigrade, in an atmosphere of nitrogen, readily absorbs nitrogen and forms a product in which about 30 per cent of the nitrogen is present as barium cyanide and about 70 per cent as barium cyanamid. The reactions may be represented by the equations:

$$BaC_2 + N_2 = Ba(CN)_2$$

$$BaC_2 + N_2 = BaCN_2 + C$$

It was further found that on fusion of this mass with soda the cyanamid is converted to cyanide. This mass can then be leached with water, and the cyanide solution thus obtained can be converted to sodium ferrocyanide, which is easily separated in a pure form, and which can be sold as such or be converted into pure sodium cyanide by fusion with metallic sodium.

The interruption in the production of gold in Africa, due to the Boer war, caused a decline in the price of cyanide, which stimulated the search for cheaper methods of production. It was found that calcium carbide could not only be manufactured at a lower cost, but it had the advantage of a lower molecular weight. With calcium carbide a temperature of from 1,100 to 1,200° C. is required for absorption, but in this case the nitrogen is fixed exclusively in the form of calcium cyanamide. On fusion with alkaline salts the cyanamide is readily converted to cyanide, and this can be extracted and purified in the usual manner.

Agricultural experiments with the crude calcium cyanamid showed that this material is suitable for use as a nitrogenous fertilizer, and patents were issued in 1910 to Dr. Albert R. Frank, son of Prof. Adolph Frank, and to Herman Freudenberg, a co-worker of A. R. Frank, protecting the use of Cyanamid for this purpose. The basic patent protecting the process of manufacture of Cyanamid was issued to Prof. Dr. Adolph Frank and Dr. Nicodem Caro in 1908.

The large demands of agriculture for cheap nitrogenous fertilizer materials have directed the efforts of the manufacturers towards the production of Cyanamid rather than of cyanides and other derivatives. At present the total output of sodium cyanide derived from Cyanamid is only about 2,000 tons per annum, while the world's production of Cyanamid is estimated at about 120,000 tons per annum.

MANUFACTURE OF CYANAMID.

Calcium cyanamide is formed in accordance with the equation

$$CaC_2 + N_2 = CaCN_2 + C.$$

The raw materials, therefore, are calcium carbide and nitrogen. Calcium carbide is formed in accordance with the equation

$$CaO + 3C = CaC_2 + CO.$$

The raw materials for this reaction, therefore, are lime and coke.

For the production of carbide, lime, from 1 inch to 2½ inches in size, and coke, about ½ inch, are mixed, in the proportions demanded by the equation, to produce a carbide about 80 per cent pure. The mixture is shoveled continuously into a 3-phase electric furnace. The furnace consists of a supporting base and four retaining brick walls which are filled with the lime and coke mixture, into which is submerged three carbon electrodes carrying the current. The resistance of the materials to the passage of the current raises them to a temperature at which the lime melts freely and combines with the coke to form liquid carbide. At intervals, as the carbide accumulates, it is tapped off through a suitable tapping hole at the side of the furnace into iron cars. After cooling, the carbide is crushed and ground to a fine powder, and is then packed in perforated cylindrical steel cans in the axis of which is a cylindrical paper core. The can with the

*Address before the Nashville Section of the American Chemical Society, November 15, 1912.

carbide is set in a brick walled oven, slightly larger than the can, and is covered with an iron lid. A carbon pencil is run through the paper core in the axis of the can. Upon passage of the electric current, the carbide is heated, nitrogen is admitted to the can, and the absorption takes place very readily, raising the temperature to about 1,100° to 1,200° C., at which point it is maintained until the absorption is complete. The reaction $CaC_2 + N_2 = CaCN_2 + C$ is exothermic, and the heat given out is almost sufficient to maintain the mass at the combining temperature. Upon completion of the reaction the cans are removed and the product is allowed to cool. It is a bluish black solid, containing small glistening crystals of pure calcium cyanamid.

PREPARATION.

The nitrogen required for the manufacture of cyanamid is separated from the air by either the liquid air process or the copper oxide process. The latter is in use at present by the American Cyanamid Company. The copper oxide process is based upon the ease with which heated copper combines with oxygen. The very finely divided copper suspended in a mass of asbestos or other inert material is contained in boiler shells provided with means for supplying heat externally. Air is pumped through the retort, which is at about 800° C., and is completely deprived of its oxygen. The nitrogen is then freed from carbon dioxid by passage through a caustic soda tower. The moisture is removed by refrigeration, followed by passage of the gas through layers of lime, and finally through calcium chloride. The nitrogen must be pure and dry, since otherwise there is a destruction in the nitrifying ovens of the carbon pencil and of calcium carbide in accordance with the following reactions:

$$C + O = CO$$
$$C + H_2O = CO + H_2$$
$$CO + CaC_2 = CaO + 3C$$
$$CO_2 + 2CaC_2 = 2CaO + 5C$$
$$H_2O + CaC_2 = CaO + C_2H_2$$
$$3O + CaC_2 = CaO + 2CO$$

The oxidized copper in the nitrogen separation retorts is reduced in place by reducing gases, such as natural gas.

PREPARATION FOR USE AS A FERTILIZER MATERIAL.

The crude cyanamid obtained from the nitrifying ovens, after cooling, is crushed to a fine powder, and is passed into rotating, slightly inclined, steel cylinders, in which it is treated with sufficient water to eliminate the carbide and to slake the calcium oxide. A further slight addition of water is made before the material is run through briquetting machines.

The resulting bricks harden rapidly and are stored until they can be crushed just prior to shipment. Crushing is done in a series of rolls with intermediate screens, the final product having a coarseness of about 15- to 50-mesh screens. It is packed in ordinary fertilizer bags and distributed in carload lots to manufacturers of mixed fertilizers. The material so prepared contains nitrogen equivalent to about 19 per cent ammonia.

It analyzes approximately as follows:

Calcium Cyanamid	45%	Iron and Alumina	2%
Calcium Carbonate	4%	Silica	2%
Calcium Hydroxide	27%	Combined water	4%
Calcium Sulphide	1%	Free moisture	1%
Free Carbon	14%		

USES OF CYANAMID.

At present, cyanamid is used in this country principally for agricultural purposes. It is known to have a fertilizing value equal or superior to that of other common products used for the same purpose. Some of the earlier experiments with this material indicated an uncertain action on very acid moor soils, but the same thing is true of other fertilizers requiring nitrification prior to absorption by the plant, and is the fault of the soil and not of the fertilizer. Such soils must be restored to normal condition before fertilizers can be expected to have their full effect. In other cases, experimenters applied quantities far in excess of those used in practical agriculture, and obtained a lower efficiency of utilization than with the normal applications. As a general conclusion from the hundreds of recorded experiments and from the testimony of practical agriculturists, it may be said that when Cyanamid is used in the same way as other fertilizers are used in ordinary practice, its efficiency of utilization is about the same as that of the high-grade fertilizer materials, and superior to that of the low-grade fertilizer materials.

The particular advantage of cyanamid as a fertilizer material lies in the advantageous effects that follow its admixture with other constituents of complete fertilizers. It greatly improves the mechanical condition of such mixtures, and by its alkaline properties prevents the escape of valuable nitrogen oxides and of bag-rotting hydrochloric acid, set free by the action of free acids in acid phosphate upon nitrates and chlorides in the mixtures.

Statements have been made that there is a loss of ammonia from cyanamid during long-continued storage. It has been found, indeed, that the nitrogen percentage in stored material does decrease, especially in very damp climates, but it has been determined by very careful experiments, both on a small scale and on a large scale in fertilizer factories, that such decrease in the nitrogen percentage is due not to any actual loss of nitrogen, but to the increase in the weight of the material, due to its absorption of carbon dioxide and of moisture from the atmosphere. Part of the moisture absorbed is fixed chemically into forms from which it is not recovered on heating in a drying oven, hence it is necessary, when testing the storing qualities of this fertilizer, to weigh the material before and after the period of exposure and to determine the nitrogen percentage each time.

SOIL ACTION OF CYANAMID.

It has been definitely established by the researches of Ulpiani and Kappen, among others, that cyanamid applied to the soil is completely converted in the course of a few days into urea, by the catalytic action of the colloids and other constituents of the soil, in accordance with the following reactions:

$$CaCN_2 + 2H_2O = Ca(OH)_2 + H_2CN_2$$
$$H_2CN_2 + H_2O = CO(NH_2)_2$$

The urea is further converted by bacterial action and possibly by chemical processes into ammonia, which further reacts with zeolites, humates, and other soil constituents, to form double ammonium salts, that are retained as a part of the soil until further bacterial action or the solvent effect of plant roots makes them available to vegetation. Cyanamid is said to be completely utilized by the crop in from 60 to 80 days.

OTHER USES.

When cyanamid is subjected to the action of superheated steam under pressure of several atmospheres, it is converted almost quantitatively into ammonia and calcium hydroxide. It thus serves as a convenient and cheap source of pure ammonia. By the Ostwald process, which uses thoria and ceria as catalytic agents, ammonia can be commercially converted into nitric acid.

By fusion of cyanamid with alkaline salts in the presence of carbon, cyanides are easily produced and can be separated and purified as desired.

When cyanamid is extracted with water between 70° and 100° C., nearly all of the nitrogen is converted into dicyandiamide $(H_2CN_2)_2$. This compound is used in the dye industry and also in the explosives industry in place of ammonium oxalate, to reduce the temperature of the explosive gases.

Other derivatives, such as urea, guanidin and its salts, and various dicyandiamidin salts, are now being manufactured in Germany. One or both of the hydrogen atoms in the amide group in cyanamide, $CN.NH_2$, can be replaced by metals, alkyl or aryl groups, alcohol groups, aldehyde groups, and others, thus leading to an immense number of organic derivatives. The possibilities in this field have been investigated but little.

Various compounds of cyanamid, and its derivatives, with alkaline salts and carbonaceous materials, are made and sold in Germany under the names of Ferrodur, Intensit, Hesolin, and others. These compounds, known as "hardening" or "cementing" powders, are used in place of cyanides, ferrocyanides, waste leather and similar materials, for case-hardening of steels. These products containing cyanamid are not only cheap, but they are efficient for the purposes for which they are intended.

FUTURE OF CYANAMID INDUSTRY.

The cyanamid industry is undoubtedly only in its infancy. At present there are four factories in Germany, four in Italy, two in France, and one each in Austria, Norway, Sweden, Switzerland, Japan and America. The American Cyanamid Company built its first plant at Niagara Falls, Ontario, in 1909, beginning commercial manufacturing January 1, 1910. Additions to the plant, which will be completed in March, 1913, will give a capacity of 25,000 tons per annum, and by the end of the year the full productive capacity of the company, including the extensions now under way, should be 50,000 tons per annum.

APPLICATIONS OF DUCTILE TUNGSTEN.*

By C. G. FINK.

Less than ten years ago tungsten was universally conceded to be a very brittle metal. Since the introduction of ductile tungsten,[1] however, large quantities of drawn wire, flexible and strong, are being daily produced for the manufacture of incandescent lamps.

We have studied the physical and chemical properties of this new tungsten, and have obtained a number of very interesting results.

The ductile metal is practically insoluble in all of the common acids,[2] its melting point is higher than that of any other metal,[3] its tensile strength exceeds that of iron and nickel, it is non-magnetic, it can be drawn down to smaller sizes than any other metal, and its specific gravity is 70 per cent higher than that of lead.

It was natural that a metal with such striking properties as these should soon find applications other than that for incandescent lamps.

Electrical Contacts—Wrought tungsten has been substituted with success for platinum and platinum-iridium as contact points in spark coils, voltage regulators, telegraph relays, etc.[4] The service far exceeds that for platinum and platinum-iridium contacts, due to the greater hardness, higher heat conductivity and lower vapor pressure of tungsten as compared with platinum.

Tungsten Furnaces—These furnaces are of two types. The type recently described by Winne and Dantsizen[5] consists of an alundum tube wound with tungsten (or molybdenum) wire. To prevent oxidation the tube is encased in an air-tight box with an inlet and outlet for hydrogen. This furnace is admirably well suited for laboratory experiments. Temperatures of 1,600°-1,800° C. can be easily maintained for hours, whereas platinum at these temperatures would rapidly disintegrate.

A second type of tungsten furnace[6] is constructed on lines similar to those of the Arsem vacuum furnace. A tungsten metal tube takes the place of the helical carbon resister. The tube is surrounded by a

*Paper presented at the Eighth International Congress of Applied Chemistry, New York, September, 1912.
[1] C. G. Fink, Trans. Am. Electrochem. Soc., 17, 229; W. D. Coolidge, Trans. Am. Elec. Inst. Eng., 29, 961.
[2] W. E. Ruder, Jour. Am. Chem. Soc., 387 (1912).
[3] I. Langmuir, Trans. Am. Electrochem. Soc., 20, 237.
[4] W. D. Coolidge, Trans. Am. Inst. Elec. Eng., 31, 870; Journal of Industrial and Engineering Chemistry, 4, 2.
[5] Trans. Am. Electrochem. Soc., 20, 287.

screen and the whole enclosed in an air-tight compartment almost identical to that used by Arsem. The compartment is either evacuated or a small quantity of gas, such as hydrogen, is introduced. This furnace lends itself admirably for the study of reactions at very high temperatures, such as the production of artificial gems.

Tungsten Gauze—We have used this gauze successfully for separating solids from acid liquors. We performed these experiments on a laboratory scale. However, this gauze could well be used on a commercial scale. For example, for the removal of sludge from copper refining baths, and for centrifugal apparatus, in general, whenever acid liquids or acid gases are dealt with.

Furthermore, it might be used in apparatus such as described by Cottrell[7] for the removal of sulfuric mist from gases. The Cottrell electrodes consist of three concentric cylindrical screens of iron wire, the inner and outer ones acting as discharge electrodes, while the intermediate screen and the outer leaded glass containing vessel act as collecting electrodes from which the deposited acid drains into a leaden pan below. Tungsten gauze is not attacked by sulfuric acid and would consequently give a much longer life than iron gauze.

Wrought Tungsten Targets for Roëntgen Tubes—This application has proved to be one of the most interesting. Tungsten is very well suited for targets or anticathodes, and the realms of application and efficiency of the Roëntgen tube have been thereby greately increased.

As has been shown by Coolidge, the high specific gravity, high melting point, high heat conductivity and low vapor pressure make tungsten a far more efficient target than any other metal.

Thermocouples—We are investigating the thermoelectric properties of the couple, tungsten-molybdenum. The electromotive force increases with the temperature up to about 540°, then decreases and passes through ezro millivolt at about 1,300°. We have found this couple very convenient for high temperature measurements in the tungsten-hydrogen furnace.

Standard Weights—A material suitable for standard weights must preferably be hard yet plastic, it must not be easily scratcher nor marred, but still not be so hard that it will chip or break; furthermore, it must withstand the action of the atmosphere and finally it must be small in bulk. Now wrought tungsten can be made so hard that it will readily scratch glass and still be ductile; furthermore, the density is high (19.3 to 21.4) and it is unaffected by the atmosphere. Tungsten weights remain wonderfully constant.

Tungsten Cells—We have taken up the study of the electrochemical behavior of tungsten and have made up a series of cells and combinations. All measurements were made at 25° and compared with the calomel electrode as standard. Our readings for the cell tungsten, aqueous sodium hydrate, potassium chloride, calomel, mercury are:

5 N NaOH, 0.68; 2 N, 0.62; N, 0.57; $^1/_5$ N, 0.525; $^1/_{10}$ N, 0.50; $^1/_{20}$ N, 0.48; $^1/_{40}$ N, 0.455; $^1/_{160}$ N, 0.445; $^1/_{320}$ N, 0.380; and 0.0 N, 0.06 volt. In the last cell the tungsten rod was immersed in distilled water.

The addition of small amounts of impurities to the tungsten metal causes the tungsten—sodium hydrate electrode to assume E. M. F. values that approach that of zinc in zinc sulfate.

The values for potassium hydrate are similar to those for sodium hydrate. The E. M. F. of the cell $Hg—Hg_2W_3O_{11} + Na_2WO_4$ solid—Na_2WO_4 sat. soln. —solid $Na_2WO_4—W$ was found to be 0.505 volt and promises to be a good standard cell.

Miscellaneous Applications—Besides the applications of tungsten cited above, many others have been but partly worked out and others merely suggested.

Owing to its chemical stability, the finest sizes of wire down to 0.0002" or 0.005 mm. in diameter are well adapted for galvanometer suspensions and for cross hairs in telescopes. It has also been suggested to use these fine wires in surgical operations in place of the coarser gold and silver wires. A further suggestion is the use of the wire in musical instruments. The tensile strength and elasticity of tungsten wire are exceptionally high (see table below).

It could be used to advantage in climates where steel is readily corroded.

We are investigating the formation of hydrocyanic acid gas by passing over heated tungsten wire mixtures of nitrogen and acetylene or methane.[8]

The heat of formation of HCN is: $C_2H_2 + N_2 = 2HCN - 9400$ cal.

We are making acid-proof dishes and tubes out of tungsten. Furthermore, tungsten wire recommends itself as a unit resistance, since it can be made absolutely pure, can be easily duplicated and is not corroded.

Since Tungsten is non-magnetic and elastic, it is being tried out in electrical meters, replacing the phosphor-bronze springs.

Similarly, watch springs could be made which would never become magnetized. Finally, we might mention: tungsten pen points, tungsten drawing dies, tungsten knife blades, tungsten reinforced asbestos curtains and fireproof coverings, etc.

Starch flour manufacture from sweet potatoes is reported as a developing industry in Umvoti County of Natal, South Africa. During 1912 over 150 tons of it were exported to Great Britain, where it brought $50 to $55 per ton.

[7] U. S. patent 1,006,620.
Journal of Industrial and Engineering Chemistry, 3, 542.

[8] Compare Berthelot and Lipinski, Z. Elektrochemie, 17, 287.

METHODS OF ANALYSIS USED IN THE LABORATORIES OF THE ARMOUR INSTITUTE OF TECHNOLOGY.

Mineral Analysis of Water.

The water, if turbid, must be well shaken before samples are taken for any determinations and 250, 500 or 1,000 cc. samples, depending on the solids in solution, filtered through a weighted filter paper. This is washed slightly with water dried at 105° and weighed as total suspended matter. It may also be ignited and weighed as inorganic suspended matter.

Total Solids: The filtrate is evaporated to dryness in a weighed platinum or silica dish over a water bath, sand bath or asbestos board. Any method is applicable till a small volume is reached, as long as the water does not boil and spatter. The final evaporation must be at 100°. When constant weight is obtained, the dish may be gently ignited to obtain the total mineral solids. Should there be a large residue of carbon, the ignition must be stronger to remove it. The residue must then be moistened with a solution of ammonium carbonate and the excess ammonia driven off. The total solids, loss on ignition and total inorganic solids should be recorded from these determinations. It is well to note the presence or absence of fumes and intensity of charring during ignition.

Silica: The residue is moistened with concentrated HCl, evaporated to dryness and baked on the sand bath from 15 minutes to one-half hour. It is then taken up with 3/4 cc. 1 : 1 HCl and 40 cc. water and digested a few minutes to take all soluble matter into solution. It is then filtered and washed free from chlorides. The precipitate is ignited in platinum and weighed as SiO_2. If the quantity is large it should be volatilized with hydrofluoric acid and a drop of sulphur; and the crucible again ignited and weighed. The loss in weight is SiO_2. The residue in the crucible should be fused with $KHSO_4$, dissolved in water and added to the filtrate. This volatilization is unnecessary with all ordinary waters.

Iron and Alumina: The filtrate is boiled with a few drops of nitric acid to oxidize the iron, made slightly alkaline with ammonia and the excess boiled off. The solution is filtered and washed thoroughly with hot water. The precipitate is ignited in platinum and weighed as Fe_2O_3 and Al_2O_3. For all ordinary purposes, it is unnecessary to separate them, but for special purposes, such as paper-making, etc., it is necessary to know the iron content of the water. In such a case, the oxides are fused with $KHSO_4$, the melt dissolved in water and dilute H_2SO_4. The iron is reduced with zinc and titrated with permanganate in the usual way. The iron so obtained may be calculated to the oxide and subtracted from the total weight to give Al_2O_3.

Calcium: The filtrate from the iron and alumina is heated and ammonium oxalate solution added till no more precipitate forms. It is digested 15 minutes or one-half hour, tested with oxalate for complete precipitation and filtered. It is washed well with hot water, but if it is to be titrated, must be washed free from chlorides. If it is to be ignited six washings are sufficient. The precipitate and paper may be ignited, preferably in platinum, at the blast lamp temperature, for about a half hour, and weighed as CaO. Or it may be dissolved in dilute sulphuric acid and titrated with permanganate. The iron value divided by 2.0 gives the CaO value of the solution.

Magnesium: In case excess of ammonia salts have been used or if the highest accuracy is desired, the filtrate from the calcium should be evaporated to dryness with a little HCl and heated to the cessation of white fumes. The residue is taken up with a very little HCl and hot water, and filtered if at all cloudy. It is cooled and a solution of sodium ammonium phosphate in excess added. Five to ten cc. of 10% solution is usually sufficient. The solution is then made alkaline very slowly with ammonia and stirred constantly. At the end of five minutes, fifteen to twenty cc. strong ammonia should have been added and the crystalline precipitate commenced to settle out. In case of haste, this may be shaken vigorously for fifteen minutes to complete the precipitation, but it is best to stand over night. It is filtered and washed with dilute ammonia. Filter and precipitate are ignited in *porcelain*, gently at first and then at a white heat. The MgO is calculated from the $Mg_2P_2O_7$ by the factor .3624.

Optional Method for Magnesium: There is also an optional method for magnesium which is fairly accurate, but very quick, and may be used to check other results in case of suspicion of error. One hundred cc. of the water, accurately measured, are heated *nearly* to boiling and titrated to an exact end point with N/10 HCl using methyl orange as indicator. It is then boiled to remove the CO_2 and placed in a 200 cc. flask to which water must be of known standard about N/10. The flask is shaken thoroughly, cooled under the tap and diluted to the mark and again shaken. The precipitate is allowed to settle, and 100 cc. of the clear top solution drawn off and titrated with N/10 HCl using plenolphthalein as indicator. The

difference between the acid required to neutralize the lime water according to standard, and that taken in the determination, gives the amount required to precipitate all the $Mg(OH)_2$. One cc. N/10 equals .0020-18 MgO. The iron or alumina present act as Magnesia and must be subtracted by proper calculation.

Sulphuric Acid: A fresh 250 cc. sample of water, filtered if necessary, is made distinctly acid with HCl, evaporated to about 150 cc. and excess $BaCl_2$ solution added. The precipitate is digested for some time, filtered through barium sulphate paper and washed free from chlorides. The precipitate and paper are ignited in porcelain.

$$BaSO_4 \times .34293 = SO_3.$$

Alkalies: The filtrate is made slightly alkaline, with ammonia, ammonium oxalate solution added till no further precipitation occurs, and ammonium carbonate solution in the same way. The precipitate is digested a few minutes and filtered and washed thoroughly. The precipitate is discarded. The filtrate is evaporated to dryness, preferably in platinum, though a casserole will answer the purpose. The ammonium salts are then completely expelled by heat, although the dish must never go above the very dullest red. When no more white fumes are evolved, the dish is allowed to cool, the residue is taken up with a few cc. of water, a drop of ammonia, and a similar quantity of ammonium oxalate and ammonium carbonate. The precipitate is allowed to form over night, or four hours at least, the solution filtered into a weighed platinum or silica dish. After thorough washing with as little water as possible (very small funnel and paper used), the filtrate is evaporated to dryness and the ammonia salts expelled by gentle heat. Care must be taken not to heat any part of the dish above a dull red. The heating is repeated till constant weight is obtained of the NaCl and KCl. These salts are dissolved in minimum water and sufficient platinum chloride solution added, calculated from the weight of salts. One cc. of 10% solution is sufficient for 30 mgm. salts. This solution is evaporated to a sirupy condition and 25 cc. of 80% alcohol added. The residue is stirred with a rubber-tipped rod until all the crystals are broken up and settled clear. After standing a few moments, the clear solution is decanted off, leaving the heavy yellow crystals of $K_2P + Cl_6$ in the bottom of the dish. These crystals are washed with more alcohol by decantation and dried at 100°.

The chemical factors used for calculation:

$$K_2P + Cl_6 \times .30712 = KCl.$$
$$K_2P + Cl_6 \times .19411 = K_2O.$$
$$NaCl \times .53077 = Na_2O.$$

Carbonates: Two hundred and fifty cc. of the water are heated *nearly* to boiling and titrated with N/10 HCl using methyl orange as indicator. One cc. N/10 acid equals .0022 CO_2.

Chlorides: Fifty cc. of the water are titrated with silver nitrate solution (2.3944 gm. per liter), using 1 cc. of 10% K_2CrO_4 solution as indicator. The water, if excessively acid or alkaline, should be neutralized before titration. One cc. $AgNO_3$ equals 10.0 parts per million (.0005 gm. Cl) on a 50 cc. sample.

Free CO_2: One hundred cc. of the water are titrated to a permanent pink with N/10 Na_2CO_3. The reaction is slow but accurate.

1 cc. N/10 carbonate = .0022 CO_2.

Calculating Results.

The mineral analysis of the water having been completed, the next procedure is the calculation of the results. The constituents as determined in the water must be calculated to the condition in which they probably existed in the water. This is in many instances as important, perhaps more so than the accurate analysis of the water itself.

In our laboratories we prefer the method in use by the Illinois Water Survey, in which the calculations are made starting with the most soluble compounds present in the water. The constituents in an average water, in order of their solubility, would be potassium nitrate, potassium chloride, potassium sulphate, sodium nitrate, sodium sulphate, sodium chloride, magnesium chloride, magnesium sulphate, magnesium bicarbonate, calcium chloride, calcium bicarbonate, calcium sulphate.

You will note that these compounds are not absolutely in order to their solubility. We make our calculations complete say on the salts of the one base before taking the next base. This means, quite often, that some compounds a little less soluble than others will be calculated first.

As an illustration of the way in which this method of calculation is applied, an analysis is given in which are stated the constituents as determined and the compounds calculated from these constituents.

Constituents as determined:

	Parts per million.
Silicon dioxide	24.00
Oxides of iron and alumina	7.00
Calcium oxide	202.40
Magnesium oxide	67.26
Sodium oxide	241.56
Potassium oxide	19.00
Sulphur trioxide	375.20
Chlorine	147.50
Carbon dioxide	107.80

The constituents probably existed in the water as:

Silicon dioxide	24.00
Iron and aluminum bicarbonate	16.00
Potassium chloride	29.10
Sodium chloride	220.90
Sodium sulphate	339.80
Magnesium sulphate	201.78
Calcium sulphate	32.15
Calcium bicarbonate	498.10

Mineral production in the United States reached an aggregate value of $1,918,326,253 in 1911, against $1,000,000,000 12 years ago and $500,000,000 25 years ago.

DETERMINATION OF IODINE IN SEA-WEED.

By HENRIK KNUDSEN.

In the research work, carried on at present by the Bureau of Soils on the Pacific coast sea-weed, the greatest fault seems to be in the quantitative determination of the valuable inorganic substances found in the different algae.

Naturally, an examination of the habitat of these marine plants along the shore is, in the first place, a necessity; however, it is of no less importance to make just as satisfactory and accurate analysis of these plants, both qualitative and quantitative. The inorganic contents in sea-weed always depend upon the local physical conditions under which the plant grows. Even in the same species, the percentage of the valuable materials vary considerably, depending upon the location. Moreover, each separate part of the coast has its special species. Nevertheless, any given species of the same yearly class, grown at a given place and hence under the same physical conditions, always possesses a nearly constant composition of inorganic substances. This is best shown by the percentage of iodine in the algae.

The Bureau of Soils has used in the analytical determination of valuable inorganic substances—especially iodine—methods which can safely be said not to be wholly reliable.

When iodine is to be determined quantitatively in sea-weed or in the ash of sea-weed, it needs must occur in relatively small quantities from traces up to ½ per cent. The differences are, however, altogether too great to allow a calorimetric determination to give a dependable result, more so since an error of 0.1 per cent in the determination of this valuable constituent may decide whether the marine plant is to be of technical use here in the future or not—independent of the richest percentage of potash that may be possessed by that plant.

In the determination of these small quantities of iodine in sea-weed, the Bureau of Soils has made use of the so-called "Permanganate Method." Any expert in this field knows that this method, as it commonly occurs, requires that the samples be free from any admixtures of organic matters, sulphides and sulphites. The sea-weed, which has been "incinerated and extracted," as reported in the Senate Document, can, however, contain considerable quantities of these various substances.

METHODS FOR DETERMINING PERCENTAGE OF IODINE.

Below I propose to give a few methods by which the percentage of iodine in the ash of the sea-weed can quickly and accurately be determined, and which are not influenced by the presence of organic matters or other oxidizable compounds nor by the presence of chlorides and bromides. In a following paragraph is given a method of incinerating the sea-weed in order to assure of a reliable determination of iodine in the plant itself.

A portion of 20 grams of the given sample (sea-weed ash) is extracted with boiling water in a beaker or Erlenmeyer flask, and the extraction filtered over into a 500 cc. flask. The residue is extracted several times, the liquid in each case being added to the filtrate in the flask. Finally the filter is washed with boiling water until a few drops no longer give an "iodine" reaction with starch and bromine water or a "haloid" reaction with silver nitrate and nitric acid. After cooling, the flask is filled to the mark and the contents thoroughly agitated. In suitable measured portions of the above alkaline solution the percentage of iodine can be determined by the methods of Duflo, Lasseigne or Groeger.

DUFLO'S METHOD.—In the determination of iodine, according to this method, a portion of 50 cc. is used, which corresponds to 2 grams of the above extracted sea-weed ash. The iodine, contained therein, is liberated by an excess of diluted sulphuric acid, after the addition of sufficient ferric sulphate to free all the iodine present.

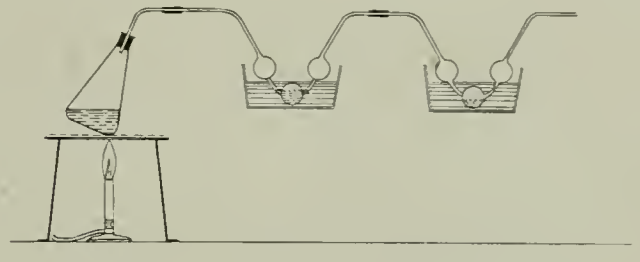


Fig. 1.

$$2\,KI + Fe_2(SO_4)_3 = 2\,Fe\,So_4 + K_2\,SO_4 + I_2$$

The ferric sulphate used is usually in the form of iron-potassium alum (25-30 cc. in a 1:5 solution).

The boiling of the mixture can be effected in a 200 cc. Erlenmeyer flask, which is heated in an inclined position on iron netting. To promote a vigorous boiling, a few pieces of pumice-stone should be introduced into the flask. The liberated iodine sublimes and is absorbed by a 10% KI solution, placed in a pair of "bulb tubes," which are connected in such a manner that the "bulb tubes" make air-tight connections with each other and the flask-connection, and do not permit the iodine vapors to come in contact with the rubber of the connections. The "bulb tubes" are kept at a lower temperature by cold water baths. (Fig. 1). The boiling should be kept up some time after one fails to perceive the violet vapors in the apparatus, in order to make sure that all the iodine has been driven out of the flask. To make sure that all iodine is expelled, the apparatus is disconnected and a strip of paper moistened with starch solution is held in the escaping vapors from the distilling flask. To prevent the liquid in the tubes from being drawn back, the burner should not be removed until the flask has been disconnected from the rest of the apparatus. The

[1] Senate Document 190—62d Congress, 2d Session.

contents of the "bulb tubes" is transferred to an Erlenmeyer flask and the free iodine titrated in the usual manner with $\frac{N}{10}$ $Na_2S_2O_3$.

To overcome any sources of error in the sublimation, some years ago I constructed the so-called "Landmark apparatus." Each part of this apparatus fits airtight into its proper place. Moreover, it has the advantage that the tranference of the KI + I mixture into another vessel is obviated, since the titration is made in the same flask, where the liberated iodine was absorbed (Fig. 2). Only the conducting tube (c) and the small bulb tube (e) need be washed out. In the absorption flask, there must not be more KI solution (1:10) than is required to make the end of the conducting tube just touch the surface of the liquid. The large bulb on this tube will effectually prevent any drawing back of the liquid into the flask (a).

This apparatus is extensively used abroad for determinations of chlorine, bromine and iodine. It can be obtained from any dealer in chemical apparatus.

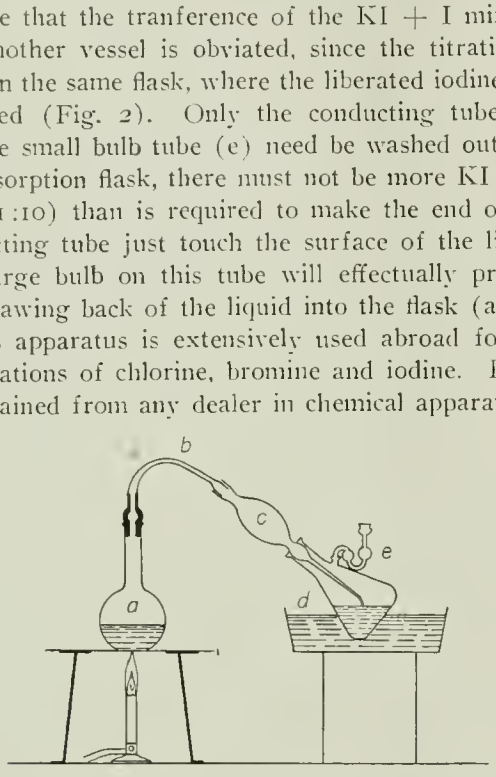


Fig. 2.

Lassaigne's Method; Palladium Method. — A portion of 25 cc. of the above mentioned solution of the sea-weed ash is diluted with water and boiled 3 or 4 minutes to expel the present free H_2S. It is then cooled and the solution acidified with dilute hydrochloric acid and put in a warm place (30-40° C.) for about 24 hours until the solution no longer smells of H_2S, liberated from sulphides present in the ash.

Any sulphur liberated is filtered off. The iodine is then precipitated by addition of a palladous-chloride ($Pd\ Cl_2$) solution (containing one gram metallic palladium per 150 cc. solution) in the form of $Pd\ I_2$. After allowing the precipitate to settle, it is collected on a filter which has been dried at 100° C. and weighed accurately. The precipitate is then washed and dried at 100° C. From the weight of the palladous iodine ($Pd\ I_2$) is calculated the percentage composition of iodine.

Groeger's Method.[2]—This method is based on the fact that when the iodides of the alkaline metals in neutral or alkaline solutions are boiled with a solution of $KMnO_4$ (1:25) they are completely oxidized into iodates while the present chlorides and bromides suffer no change at all, as for example:

$$KI + 2KMnO_4 = KIO_3 + K_2O + 2MnO_2.$$

The quantity of iodine present over 50-100 milligrams is not desirable in this method.

A suitable quantity for the determination of iodine in kelp-ash is 100 cc. of the above-mentioned extraction (corresponding to 4 grams of the ash). To this when boiling is added enough permanganate solution until the liquid above the precipitated MnO_2 appears distinctly red in color. The excess of $KMnO_4$ is reduced by adding alcohol drop by drop until decolorization has taken place. The precipitate is now filtered out by a double filter and carefully washed with cold water. To the filtrate, which now contains all the oidine in the form of potassium iodate, is added 10-15 cc. of a 5 per cent solution of KI, and it is then acidified with H_2SO_4 (1:4). All the iodine is liberated according to the formula:

$$KIO_3 + 5KI + 3H_2SO_4 = 3K_2SO_4 + 3H_2O + 6I.$$

Since the liberated iodine is six times as great as that to be determined after titration with $\frac{N}{10}$ $Na_2S_2O_3$, 1 cc. will correspond to $\frac{126.92}{6} = 0.0021153$ gram of iodine.

Considering Groeger's method as a whole, it is worthy of mention, that if the chlorine compounds of ammonia be present, the potassium oxide (K_2O) formed will liberate NH_3, which afterwards through oxidation can give rise to KNO_2. When the solution is acidified, the nitrous acid (HNO_2) formed will separate additional iodine from the KI which was added, evidently giving too high a result of iodine. One can guard against this by, previous to the oxidation with the $KMnO_4$, adding an excess of NaOH and boiling out all the ammonia.

In comparing the results obtained by these three methods I will append the following results obtained in determining the iodine contained in different samples of Norwegian kelp:

Sample.	Duflo's method.	Groeger's method.
1.	1.322% I	1.395% I
2.	1.228	1.271
3.	1.473	1.540
4.	0.817	0.876
5.	0.375	0.445
	Groeger's method.	Palladium method.
6.	1.012% I	1.024% I
7.	1.645	1.740
8.	1.160	1.210
9.	1.380	1.450
10.	1.120	1.120

On the average, the difference between the results by Duflo's and Groeger's methods is 0.062 per cent and between Groeger's and the Palladium method 0.045 per cent, Groeger's method giving slightly higher values than Duflo's and slightly lower than the Palladium method.

[2] Feilschrift für angewandte Chemie, 1894.

RESUME OF METHODS.

Duflo's Method.—The determination of iodine is rapidly made, but the sublimation demands a constant attention. It is moreover difficult to get the last of the iodine to distil over, without the risk of having the KI solution drawn back. Hence the results are apt to be too low and two portions of the same ash seldom give absolute agreement in results. Landmarks apparatus has in this respect been a great improvement.

Lassaigne's Method (Palladium Method).—This method gives rather accurate results, but it takes time, hence, as a rule, it will be impracticable in factory laboratories.

Groeger's Method.—This method is simple; it demands no special apparatus and—as is shown by present analyses—gives results which closely approximate those of the Palladium method. On account of the titration and washing it requires somewhat more time than Duflo's, but these operations can be expedited if a vacuum pump is at one's disposal. No special attention is needed, and several analyses can be carried on at the same time. The results nearly always agree among one another.

Groeger's method deserves to become known in this country, and it will probably be entered in the new U. S. P. for the determination of iodine in thymoliodide. For this purpose I have used the method for years with good results.

As is known, previous to this there have been difficulties in obtaining absolutely satisfactory results in the use of other methods. For the purpose of the U. S. P., Groeger's method has undergone a simple modification at the laboratory of Powers, Weightman Rosengarten Co.

This method is also well adapted for the determination of iodine in commercial iodine and should likewise be entered into the U. S. P. One-half to one gram of iodine is dissolved in a strong solution of 0.5-1.0 gram of NaOH in water. When all the iodine is dissolved, the solution is poured into a 250 cc. flask, which is then filled to the mark and well shaken. The amount of iodine in 25 cc. of this solution is then determined by boiling with $KMnO_4$, etc.

The presence of chlorine and bromine in the iodine will not affect the results, but which, on the other hand, will be the case when one proceeds in the customary way of titrating the iodine in a KI solution, since Cl and Br will then liberate I from KI. Hence in titrating with $\frac{N}{10}$ $Na_2S_2O_3$ the result will be found in excess of the true value.

THE SEA-WEED'S COMMERCIAL VALUE IN INORGANIC MATTERS AND ITS BURNING TO ASH (KELP).

It is now a well-known fact, that the amount of valuable substances in the marine plants varies with the time of the year. It is also well known that the same species growing on different parts of the coast can have a different composition in inorganic substances, and that the same species varies considerably in that respect, depending on the latitude. It also depends in the first place on the physical conditions under which the plants grow. To assign a universal and absolute technical or economic value for a long coast line is therefore an impossibility, while in each separate case it can only be determined by chemical analyses. If the sea-weed is incinerated and occurs in the form of ash, it will each time be comparatively easy to determine the commercial value of this raw material.

It is, nevertheless, often important to become acquainted with the original percentage of valuable organic and inorganic substances in the case of the separate species, but to gain a satisfactory knowledge of them presents practical difficulties in many respects. The main difficulty lies in the transportation of well-preserved samples long distances to the laboratory, which is the only place where this part of the examination of the sea-weed can finally be undertaken. As a rule one will find lower results, especially in iodine and actual potash, in the plants incinerated in the laboratory, than in the same plant incinerated where it was gathered from the sea in a fresh state. This also appears in that fact that the yield of ash is greater in the second case. The reason for this is apparent. If the samples of the marine plants be transported in a fresh moist condition a rather long distance, they will ferment and a part of the inorganic salts will escape in the liquid of fermentation. If, on the other hand, they be transported in a dried condition, many of the present salts will crystallize out of the plant and be lost in this way. Hence, in the physical research work on the Pacific coast the experts when in the field should always have with them a portable laboratory, which should be equipped with the necessary apparatus for a general preliminary examination of the plants, with respect to its percentage composition of water, ash, the solubility of the latter, etc., as a check and comparison of the samples taken. When these are to be forwarded, they should only be half-dried, and then packed in paraffined pasteboard boxes to obviate an excessive drying of the plants en route.

Of such a half-dried sample, a portion of 50-100 grams is weighed out and placed in a platinum dish, where it is dried at 110° C. to constant weight. This weight is taken as the initial point in the determination. The dish is now heated over a Bunsen burner until the contents is thoroughly charred. During this process the contents of the dish is carefully stirred with a glass or platinum rod and the heat should not exceed dull red.

When the charring is completed the charred residue is extracted with boiling water and the liquid filtered over into a 500 cc. flask. After a suitable washing with hot water, the residue and filter are put back into the dish, dried again and all the char is burned up by ignition until it is obtained as a grayish white ash. The residue is again lixiviated with hot water, the ex-

traction filtered into the 500 cc. flask and the new filter and the residue is incinerated as before. The ash is now weighed carefully.

After cooling, the flask is filled to the mark and shaken up repeatedly. In 100 cc. of the liquid, the soluble salts are determined, after evaporation on water bath and drying at 110° C. From these soluble salts and the ash above is calculated the total amount of ash in the marine plants (that is, "kelp").

For illustration, I have appended below the percentages of ash of several different species of algaes (dried at 110° C.) occurring on the coasts of Norway. I have included the per cent of iodine in each case, to illustrate the intrinsic values of the different species. The amount of valuable substances decreases obviously with the decrease in amount of ash, while a marked increase in insoluble matter exists in the marine plants which contain little valuable matter:

Species.	Per cent of ash.	Per cent of iodine.
Laminaria digitata	25.26	1.32
Laminaria chustani	26.76	1.12
Laminaria saccharina	15.82	0.64
Fucus siligulasus	14.48	Traces
Fucus ascophyllum nodosum	13.23	Traces
Fucus veciculasus	12.24	Traces

In the incineration of the "drift sea-weed" great care must be exercised, for when this marine plant is thrown upon a sandy shore by the tide or breakers, it will be found that grains of sand cling to it. When incinerated the SiO_2 of the sand will at a higher temperature (red heat) liberate a part of the iodine contained in the plant.

The whole plant of the Norwegian Laminaria digitata grown at sea yields, upon careful incineration, as above mentioned, from 4.5 to 5.7 per cent ash. This ash containing from 78-85 per cent soluble salts, 28-35 per cent actual potash (K_2O) and 1.5-2.8 per cent iodine.

After a 26-year campaign the United States Geological Survey has received generous recognition at the hands of Congress in the authorization of an expenditure of $2,596,000 for the construction of a fireproof building "of modern office-building type of architecture." With this sum it is proposed to erect a building on ground already owned by the government which shall accommodate, besides the Geological Survey, the Reclamation Service, the Indian Office, and the Bureau of Mines, all bureaus of the Interior Department whose work is closely related to that of the survey and among all of which there is more or less constant co-operation. The public buildings law, which carries the survey item, authorizes an immediate appropriation of $596,000, the balance to be appropriated as needed in construction. While this omnibus building law is only an "authorization" measure, leaving the actual appropriation of the money to a future act, $96,000 of the amount included in the measure can be expended immediately, having been appropriated by a former Congress in connection with the purchase of the site on which the survey building is to be erected.

AN ELECTRIC HEATER FOR LABORATORY DISTILLATIONS.*

By L. T. BRYSON.

While the heater described below was designed only for naphtha and turpentine distillations, it has been found so useful for miscellaneous extraction work, moisture determinations, etc., that details of its construction may be of interest. It may be set up in almost any laboratory with very little expense.

A steel can 4½ inches in diameter and 9 inches

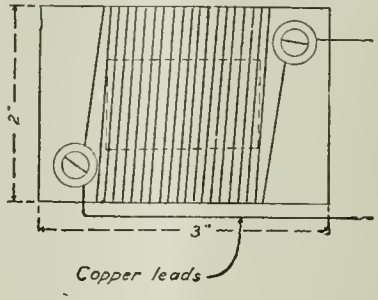


Fig. 1. Detail of Element.

high, with a ⅜ inch vertical slot cut half-way down the side, is lined with a double thickness of 1/16 inch asbestos paper. About ⅜ inch of loose magnesia is placed in the bottom and covered with a circular piece of heavy asbestos board or transite. The can is supported on a ringstand in the usual way.

The heating element is composed of 9 feet of No. 33 nichrome wire—for 220 volts—which is wound on a block of transite ½ inch thick, 2 inches wide and 3

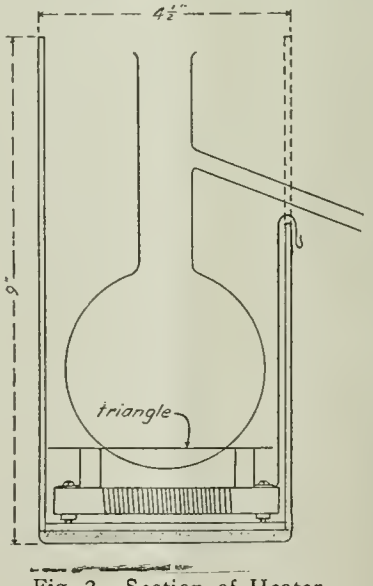


Fig. 2. Section of Heater.

inches long, having holes drilled for a bolt at each end and shallow notches cut along each of the long edges, about ⅛ inch apart, to receive the wire. To give greater effective radiation the center of the block is cut out as shown by dotted lines (Fig. 1). Each end

*From the Journal of Industrial and Engineering Chemistry.

of the resistance wire is fastened, together with the end of a piece of No. 16 copper wire, under a No. 6—32 bolt passing through the corresponding end of the block. The complete element is placed in the bottom of the can, the copper leads are brought up over the side, and connected with the line and rheostat.

A water-rheostat will prove satisfactory if a sensitive ammeter, reading in tenths up to 3.5 amperes, is at hand. In this laboratory, a rheostat provided with 18 points is used, with 5 feet of No. 30 nichrone wire per point. The wire is conveniently wound on short pieces of iron pipe insulated with asbestos.

With the dimensions given above, the heater will accommodate a 250 cc. flask, and gives distilling vapor temperatures up to 300° C. when the flask is supported about ½ inch above the element by means of a triangle. With the flask in place the can should be fitted with a cover perforated for the thermometer, thus enclosing the entire neck of the flask and part of the side-tube; the distillation characteristics are then very constant. With a rheostat having steps of equal resistance, as above, the temperature increment per step necessarily varies from a minimum value at the lower temperatures to the maximum value on the last points. A temperature increment which would be constant throughout the range was not considered desirable for this work.

The French company Schneider, Creusot, along with the Société des Hauts Fourneaux et Forges d'Allevard, are about to erect a large plant in Pontcharra (Isère Department), for the electrolytic production of steel.

At a meeting of the cotton section of the British Weights and Measure Association held recently in Manchester. T. R. Ellison, of Liverpool, reported on the success that they had achieved in getting the Egyptian cotton market to adopt pence and hundredths of pence in their quotations for raw cotton, thus securing uniformity with the American market. There were still some objections to be overcome in India and one the continent of Europe in the endeavor to get the system adopted for East Indian cotton. It was decided to reopen the question with railway companies and others of getting the central (100 lbs.) and the thousand weight (1,000 lbs.) adopted as standard weights in place of the present hundredweight (112 lbs.) and ton (2,240 lbs.). The former weights, it was stated, are now practically universally used in the cotton trade, and previous efforts by the committee had led to the British Government Board of Trade keeping their cotton statistics by this system —a system which practice had proved to be preferable to the hundrewieght and ton system for calculations generally. The desire of the committee now is to secure the adoption of the same system in regard to the carriage of goods and also in regard to coal, flour, and other commodities with which they deal.

THE PRODUCTION OF CHLORINE SUBSTITUTION PRODUCTS OF METHANE FROM NATURAL GAS.*

By CHARLES BASKERVILLE and H. S. RIEDERER.†

The attempts which have been made to effect a chlorination of methane in order to obtain satisfactory yields of substitution products have been discussed in a previous publication.[1] It may be noted here that while the formation of methyl chloride, dichlormethane, chloroform and carbon tetrachloride from methane has been experimentally shown by several investigators operating with various methods, and a number of processes have been patented for the production of these and other halogen derivatives of methans,[2] so far no process has been worked on a commercial scale. Since there is an abundance of natural gas containing 50-90 per cent methane in this

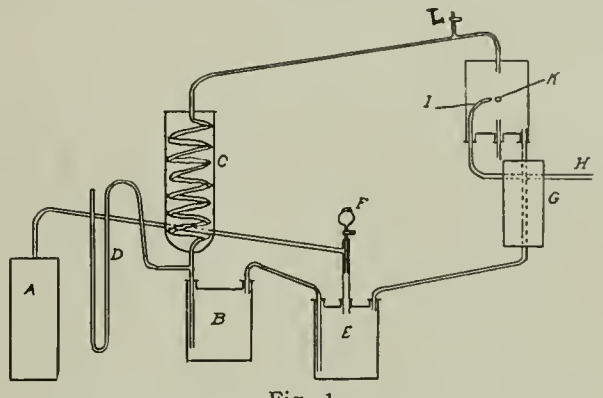


Fig. 1.

A, chlorine cylinder; B, receiver for substitution products of the reactions; C, condenser; D, pressure gauge; E, hydrochloric acid absorption chamber; F, funnel for introducing water; G, electric heater; H, tube for introducing natural gas, which plays between carbon spark terminals I-K; L, cock for releasing

country, the problem is of some importance—one which we thought would bear investigation along lines differing in certain respects from those hitherto followed.

In general, it may be said that the ultimate object of those studying the matter has been to produce a constant yield of an intermediate product. Bearing in mind the demonstration of Phillips[3] that the tendency of methane, when chlorinated, is to constantly produce either methyl chloride or carbon tetrachloride, it occurred to one of us (C. B.) that it would be more advantageous to obtain the end-product, from which, among other products, chloroform could be prepared by reduction. Accordingly a number of experiments were conducted with a view of devising a commercial process for the production of carbon tetrachloride from natural gas.

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*From the Journal of Industrial and Engineering Chemistry. Paper presented at the Eighth International Congress of Applied Chemistry, New York, September, 1912.

†The authors have filed applications for patents on the novel features presented in this paper.

[1] Baskerville and Hamor, Journal of Industrial and Engineering Chemistry, 4, 216.

[2] Mallet, U. S. patent 220,397, Oct. 7, 1879; Colin, U. S. patent 427,744, May 13, 1890; Elworthy and Lance, French patent 353,291, May 15, 1905; MacKaye, U. S. patents 880,900, March 3, 1908, and 1,009,428, Nov. 21, 1911; Walter, German patent 222,919, Nov. 5, 1909; and Pfeifer and Szaroasy, 12,058 D. Anm. P. 21,872, Sept. 25, 1911.

[3] Am. Chem. J., 16, 362.

EXPERIMENTS WHEREIN A SPARK DISCHARGE WAS EMPLOYED.

In preliminary experiments, an apparatus similar in principle to that used by Phillips was employed. It was finally decided, however, to construct an apparatus with a closed circuit, producing a circulation of the gases by heat on the rise, cooling on the drop, and recovering the products in a trap at the bottom; suitable openings being made in the apparatus for the introduction of chlorine and natural gas, and for the insertion of spark terminals in such a manner as to bring the spark in the junction line of the gases (Fig. I). Several modifications were made in this apparatus during the course of the experiments, and in the later experiments a horizontal reaction chamber (Fig. II) provided with a glass pocket for the collection of any condensation products in a liquid form

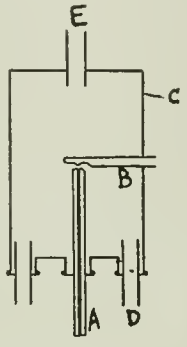

Fig. 2.

A, hollow carbon transmission tube for natural gas; this carbon is one terminal; B, solid graphite spark terminal; C, reaction chamber of glass; D, chlorine inlet; E, exit for gaseous products of reaction.

and with a hollow carbon terminal for the introduction of the natural gas[4] was used. In the experiments wherein this form of reaction chamber was used, just as in the case of the original form of chamber, bridging between the carbon terminals invariably occurred, although combustion ensued almost immediately upon starting the spark. A very small yield of products was obtained.

The first three runs, using the original form of apparatus, showed that chlorine substitution products could be obtained, although the character of the products could not he determined, owing to the small yields. The spark in these runs generally showed a dual character, partly resembling an arc and partly presenting the true color of a spark. Undoubtedly there were considerable ultra-violet rays in this latter portion.

In the runs, using the reaction chamber illustrated in Fig. II, the spark showed little of the deep blue and more of the flame. Since the gas was continuously directed into the spark, it burned continuously.

In the first three runs it is doubtful if the flow of natural gas was continually into the direct line of the spark, as no continuous flame was observed as in the runs with the modified apparatus, and it seemed reasonable to conclude that whatever chlorination was effected was through the agency of the ultra-violet rays and not by the combustion.

In all of the above experiments natural gas saturated with water was introduced into the circulating atmosphere of chlorine.

EXPERIMENTS WHEREIN UTRA-VIOLET RAYS WERE UTILIZED.

The apparatus used in the experiments which follow next was constructed as shown in Fig. III. The reaction chamber was a cruciform tube of glass, through two opposite components of which was inserted a quartz tube containing iron terminals.

In beginning, the apparatus was filled with chlorine, the heat and the spark started, and then natural gas (85 per cent methane) was admitted. The pressure variations showed that a reaction occurred, but no product could be observed except a crystalline film suspended on the water in the receiving vessel. About 5 liters of natural gas were used. Even after continuing the run for 8 hours, during which time 3½ liters of natural gas were used, no appreciable product was obtained. Accordingly, the apparatus was changed so that the natural gas was admitted below through the U-tube intended for a drain, causing it to bubble through the hydrochloric acid in the receiver.

In the next experiment, a considerable quantity of product collected in the receiving vessel: 7½ liters of natural gas were used and the temperature of the heater was maintained so low that no vapors were observed in the rising tube above the furnace. After another run, in which 3½ liters of natural gas were used, the apparatus was disconnected and the product was separated from the hydrochloric acid in the receiving vessel. Ten cc. of product were obtained; this was purified and fractionated. The first fraction came over at about 64° C., and the fractions up to 76° C. were collected. A second fraction was then taken up to 88° C. and a residue remained in the fractionating bulb. The first and second fractions were colorless and clear, while the residuum possessed a yellow color. The first fraction amounted to about 75 per cent of the total, the second and the residue to about 12.5 per cent each. These experiments showed that approximately a 20 to 25 per cent yield of carbon chlorides (chloroform and carbon tetrachloride) could be obtained from natural gas, using a circulating atmosphere of chlorine in the apparatus described.

In the succeeding experiment the apparatus was made absolutely air-tight and a thermo-electric couple was introduced into the furnace to enable temperature readings. A run was made *without* a spark. Preliminary experiments showed that but a slight reaction occurred and that the crystalline product (hexachlorethane) formed was inappreciable, although very little natural gas was used; accordingly no further experiments were made without a spark with this apparatus.

In the following run, which lasted for 8 hours, considerable product collected, and the yield seemed to

[4] Besides natural gas, methane, prepared by various methods, was used in preliminary experiments. In the following experiments, however, natural gas alone was used.

be in proportion to the natural gas used. The next runs were made after sweeping the apparatus with chlorine. After natural gas and chlorine were both

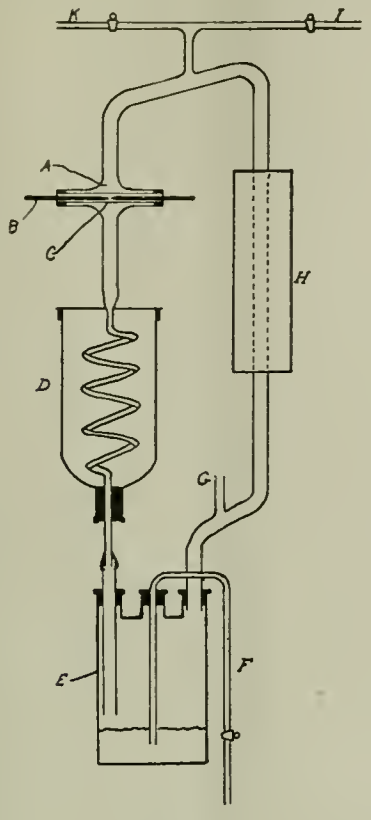

Fig. 3.

A, cruciform glass reaction viaduct; B, iron terminals; C, quartz tube containing iron terminals; D, condenser; E, receiver; F, syphon for emptying receiver; G, chlorine inlet; H, electric heater; I, natural gas inlet; K, connection to manometer.

added, the reaction proceeded smoothly, and it was finally stopped by admitting chlorine alone. The product amounted to 14 cc. from about 10 liters of natural gas; this was purified and fractionated, and was found to consists of carbon tetrachloride and a small amount of chloroform and hexachlorethane.

For the next experiments, an outlet siphon for the hydrochloric acid produced and an inlet tube for natural gas were provided in the receiver. The apparatus was completely filled with chlorine, but no heat was used in the circuit. About 4 liters of natural gas were used in each run, and considerable product was obtained; the product was not separated, owing to the fact that it was in part distributed throughout the apparatus. It was determined that the product is very sparingly soluble in hydrochloric acid and chlorine water. Attempts were made to ascertain whether the ultra-violet rays have any influence on the reaction between chlorine and methane. Beginning with daylight, the ultra-violet source was then started and observations were made on the speed of the reaction. As in the preceding experiments, the issuing natural gas was saturated with water by passage through a water bottle. However, the variations in presure were not sufficiently marked to lead one to infer that the ultra-violet rays have any effect on the reaction. In order to definitely establish this fact, a reaction chamber was constructed to accommodate an "Uviol" lamp to replace the spark section. Provisions were also made for exposing or not exposing the mixed gases to ultra-violet light, depending upon what was necessary to produce a reaction, for drying the gases by passage through sulfuric acid after the separation of the products of chlorination, and for passing the residual gases over quicklime. The form of apparatus used is shown in Fig. IV.

Beginning with a full charge of chlorine, the apparatus was run for one day and no appreciable reaction could be observed. From the experiments made, it seemed probable that the ultra-violet rays are not the necessary active rays required, for it was found that the reaction occurs in daylight, and the passage of the solar rays through glass would exclude ultra-violet light. From the observations made so far, it appeared that the solution of the problem was to find the proper

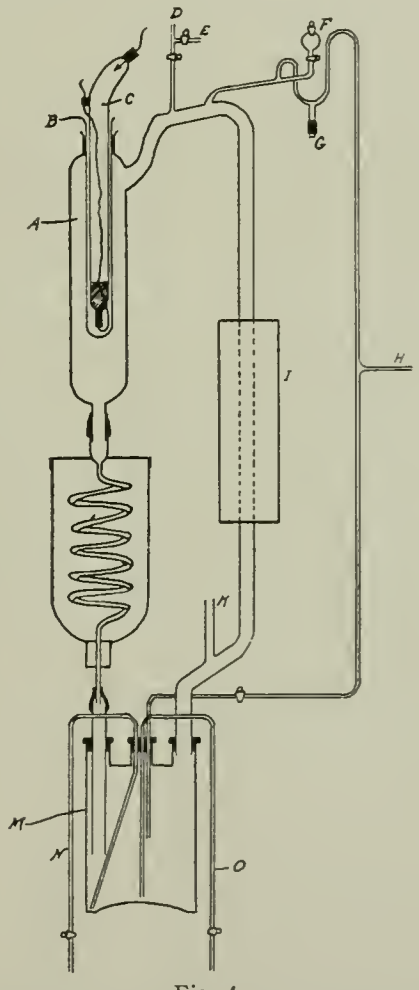

Fig. 4.

A, reaction chamber of glass; B, large thin-walled quartz tube; C, Uviol lamp inserted after current is started; D, tube connection to manometer; E, cock for releasing pressure; F, funnel for introducing water; G, trap; H, tube for introducing natural gas before or after the heater I; K, chlorine inlet; L, condenser; M, receiver; N, syphon for removing heavy products of reaction; O, syphon for removing water solution of hydrogen chloride produced in the reactions.

rays. Therefore the "Uviol" lamp was removed and the aperture closed.

A tungsten filament lamp was mounted outside of the reaction chamber, surrounded by a reflector, and no appreciable reaction occured, although runs were

made under varying conditions. Using an incandescent gas mantle containing 10 per cent of ceria, whereby the proportion of red rays was increased, with and without the aid of daylight, the reaction was practically *nil*, while with a mantle containing 3 per cent of ceria only a slight reaction occurred. With the 3 per cent ceria mantle, the reaction would take place when daylight was admitted, but would practically cease in the dark. At times a slight reaction was noted when working in the dark, but this was attributed to diffused light entering through the laboratory door. Dark here means the exclusion of daylight.

In the next series of experiments a projection lantern, using only one condenser lens and ordinary carbons, was placed in such a position as to light the upper section of the reaction chamber. The lantern was run on an 8-ampere 235-volt current, and it was shown conclusively that the arc light caused the reaction to take place. Colored screens were then interposed between the lantern and the reaction chamber, and in this manner the rays favoring the reaction were determined. A spectroscopic examination of the screens (solutions of coal tar dyes, blue, green, red and yellow, such as are used in the Pinotype color-photography outfit) showed that the blue screen passed through the green and gave but a dim indication in the deep red; that the green cut out every ray except the green with a blue fringe; and that the yellow and red screens excluded the blue end of the spectrum along with part of the green. A number of experiments demonstrated that the unscreened arc light and the arc light screened with the blue allowed a good reaction speed, while the interposition of the green, yellow and red screens slowed down the reaction almost immediately and to a considerable degree; on replacing the blue screen, however, the reaction was at once accelerated. It was found that it made little difference whether chlorine or natural gas was being run into the apparatus, except that the character of the product varied accordingly. Further experiments showed that the blue end of the spectrum is the active agent for the reaction of chlorine and natural gas. It was found that screening is of little use, since the inactive red, yellow and green rays are hardly of an interfering character. The primarily important condition was found to be a source of light rich in the rays of the visible blue spectrum—that is, the spectrum from the bluish green through the visible violet. We have found that the invisible spectrum (the ultra-violet) does not induce the desired activity and that it plays little part in the reaction.

As it was not always convenient to fuse the large glass tubes in making connections, it may be of interest to give the method resorted to for making tight junctions through which such corrosive gases as chlorine and hydrogen chloride may be passed. The glass tubes were first cut smooth and closely fitted to each other. The junction was then wrapped with wet, thin sheets of asbestos paper. After drying, the asbestos was given several coats of Bakelite varnish No. 4. The next day this was tightly wrapped with electric adhesive tape and thoroughly coated again several times with the Bakelite varnish.

PROGRESS OF WORK ON BORONIZED COPPER.*

By DR. E. WEINTRAUB.

It is usually the case that the man who contributes to the progress of a certain art is an expert in that art. I must begin my lecture, however, by frankly stating that at the time when I introduced the dexodization of copper by boron I knew mighty little about foundry and foundry matters, and that even now I could by no means qualify as an expert.

It is also usually the case that an improvement in an art is the result of considerable experimentation which either through persistent intelligent effort or through a lucky accident leads to success. No credit for great effort can be claimed in this case.

The process of boronizing copper was merely the result of a lucky idea which forced itself upon me through experimentation in a totally different line, namely, that of preparing the element boron in a pure state, a line of work which was begun primarily for the purpose of testing whether boron would be an appropriate substance for incandescent lamps.

This is perhaps a good example of the correlation of different lines of investigation and of human effort.

It demonstrates also the fact that scarcely can any truth be ascertained (no matter how abstract it may seem at a given time) which may not give practical results and help along in solving some practical problem.

The story is very short. After having isolated the element boron I was struck by the great affinity displayed by it toward practically every known element, whether metalloid or metal, but I was no less impressed by the apparent lack of affinity between boron and copper even at the melting point of the latter. I was carrying out the deposition of boron from boron chloride and hydrogen between water-cooled copper electrodes. Boron would deposit and grow on copper electrodes, but the latter would not combine with the boron, and any copper mechanically adhering to the boron could be easily washed off with dilute acids.

I had often heard that it was difficult to produce cast copper mechanically sound and of high electrical conductivity and how the accomplishing of this would be desirable for electrical and other work. I said to myself that since boron has such a high affinity for oxygen, nitrogen and oxygen-containing gases, which were probably, in one way or another, the cause of the difficulties in copper casting, and as boron on the

*A paper presented at the Annual Meeting of the American Institute of Metals, Sept. 24 to 27, 1912, Buffalo, N. Y.

other hand apparently had no affinity for copper, it was very probable that boron would be the natural deoxidizer for copper. I thought it might be worth while trying this out, but so many things look good in theory and yet do not work out in practice, and it is so hard to tell beforehand which one of a number of good ideas will work and which will be a sore disappointment, that, under the pressure of other work, I let this idea linger in my mind a number of months before I actually tried it; and then one day, when there was, luckily, a lull in other work, I asked my assistant, Mr. Kroner, to try to add a small percentage of amorphous boron (boron suboxide) to copper and see what luck he would have. He added about 0.1 per cent, and after a short time brought me a sample bar, which looked good. The same measured up to 94 per cent. conductivity of Matthiessen standard.

Surely here was an idea that worked out without much effort, and the further development of the method was just as easy as the start. Every simplification and every new idea that occurred to me was tried, and every time the result did nothing but confirm the theory.

The only difficulties I had were in trying to persuade the experts that the thing really worked and that they had to figure with a new process this time based on scientific reasoning and which had to be carried out accordingly.

The first simplification consisted in the substitution of boron suboxide flux for boron suboxide. Boron suboxide is made by reducing boric anhydride with magnesium, aluminum, or an alkali metal, and chemical treatment of the reaction product. For copper casting it is, however, unnecessary to treat the product as the ingredients of it (excess of boric anhydride and of borate) outside of boron suboxide are harmless or even useful in diluting the active agent. Of this boron suboxide flux 0.75 to 1 per cent has to be added (equivalent to 0.08 to 0.1 per cent of boron suboxide).

This is the flux at present used. However, any material which contains boron in a state of oxidation below that of boric anhydride is a flux for copper casting. Among other compounds of boron which satisfy this condition I mention boron carbide or any alloy of carbon and boron.

In order to better make the boron react on the copper, or rather on the gases in the copper, I thought it would be best to superheat the copper, and I did that, although I was told that this is equivalent to ruining the metal. The copper, I was told, would "burn." The result was as I expected.

After the process had been made to work many directions presented themselves for further investigation. First and perhaps the most important from the point of view of pure investigation was the question of what the boron flux actually does. We have no reason to doubt that the boron reduces some gas in the copper which is either oxygen itself or contains oxygen; it would be of great interest to ascertain the exact nature of the gas and the quantitative relations in the action of boron. We have not done this.

Another line was to study the deoxidation of copper alloys by boron. We have done a little on that and have ascertained that all the copper alloys containing the elements zinc, tin, lead, greatly benefit by being deoxidized by boron, but we have not done as much in this direction as we would like and as we eventually will.

Another line of work would be to study the application of the deoxidation by boron in the smelting of copper, and although a beginning was made on that in the early stages of the work it has not been pursued in any systematic way and will have to be taken up again at the first opportunity.

What we have done was influenced by the fact that the process has been developed in an electrical company. The question was what could we do with the process, what electrical apparatus could be cast and thereby either save money or improve the product. It must not be forgotten that if copper could not be cast this did not cause the electrical industry to stop still. Rather had the industry developed all sorts of ingenious ways of working copper, of drawing, punching, drop forging, etc., etc., until the methods got so perfected that when means had been found for casting copper there was, at first, hardly a place where people thought they needed it. The very same people, by the way, were always going around sighing for the time when copper could be cast, commenting what a great thing this would be.

However, by this time we have got quite a distance toward replacing forged copper by cast copper. I would point to a selection of apparatus that I have brought along which represent but a few out of the large number of castings made at present. Meter fields, coils of current transformers, transformer terminals, series coils for interpoles, blow-out coils, large current switchblades, contact studs, secondaries of welding transformers, clamps of welding transformers, etc., etc., are now being regularly cast in boronized copper. Last, but not least, I will mention the success we had in casting the rotors of induction motors, either casting the short-circuiting ring around the forged bars or casting the whole armature. I have with me one in which the whole armature is cast, and it is a nice piece of casting.

Some of these apparatus are cast in sand molds and some, of simpler shape and used in large numbers, are cast in iron molds. To the latter class belong, among others, switchblades and meter fields.

The advantages derived from the substitution of cast copper for forged copper are not only the saving in cost. In most cases, also, a better apparatus is obtained. It is possible in casting to eliminate a number of joints, which are always a source of loss in efficiency. In the case of current transformers, for instance, not only a better apparatus is obtained at a

reduced cost but also space is saved. It is considerations like these, saving of money or space, or improvement of the equality of the apparatus, that have moved the engineers to replace forged copper by cast copper in every case they have done so.

The case of the induction motor is very interesting. In this case the main advantage of the cast rotor is its indestructibility and freedom from repairs. The rotor as ordinarily built up, often develops poor contacts where the solder is applied between the forged bars and the short-circuiting ring which necessitates taking the rotor out and making repairs. As against this we had some cast induction motors run for years in very difficult places where overload was very frequent, without any need of repairs whatever.

There remains for me to give you some details of how the process of boronizing copper is carried out and what precautions are to be taken in order to secure a good casting.

The boron suboxide flux can be added to the copper in different ways which are equally good. In the Lynn foundry our pots contain about 125 lbs. of metal and up to the present coal furnaces have been used. The method used in the Lynn foundry consists in mixing half of the boron flux to be added with charcoal, putting it on the bottom of the pot and melting the copper down. When the copper has reached the necessary temperature (the copper can be heated too low but not too high) the pot is taken out, the slag skimmed off and the second half of the boron flux added and thoroughly stirred in. After a minute or so the slag comes up to the surface in the form of fused lumps and is skimmed off and the melt is cooled down by adding gates or risers until the proper pouring temperature is obtained.

In case a reverbatory furnace is used, as in Schenectady, the procedure usually followed is to put the flux in the ladle pot on the bottom, pour the copper over it and stir thoroughly.

The skimmer and stirrer are preferably not of iron, since it is difficult to avoid a solution of a slight amount of iron in the copper and a resulting lowering of conductivity. If done very carefully the amount of iron would probably be very small, but we did not find it practicable to trust the foundry men with an iron skimmer or stirrer. Heavy graphite stirrers and skimmers, made of Acheson graphite, have proven sufficiently rugged for use and are being constantly used in the foundry.

The boronizing process delivers a good metal and the production of a good casting depends now on the same factors as in other metals. The copper shrinks rather considerably, about ¼ inch to the foot, and this must be taken into consideration. The casting must be well fed and the sand mold must be rammed only very lightly. In case of iron molds the iron must, of course, be covered with soot, and in some cases it was found desirable to use a graphite plate where the hot metal first strikes. In the case of induction rotors it was necessary to overcome difficulties due to the shrinking and cracking of the different parts of the copper casting.

When these precautions are taken no more difficulty is experienced in casting copper than in casting ordinary brass.

The electrical conductivity obtained can be as high as 97 per cent of the Mathiessen standard, but in the foundry, using scrap—which is not always as clean as could be desired—we find it not feasible to guarantee more than 90 per cent conductivity.

The mechanical properties are as follows:

Tensile Strength.	Elastic Limit.	Elong.	Red in Area.
24350 lb. per sq. in.	11450 lb. per sq. in.	48.5%	74.49%
17.0 kg. per sq. mm.	8.0 kg. per sq. mm.		

The Huddersfield (England) and District Woolen Manufacturers' and Spinners' Association and the General Union of Weavers and Textile Workers have entered into the following agreement in regard to wages: (1) The classes of work people included in the settlement are men employed as dyers, laborers, millers, scourers, rag shakers and rag packers (2) Any hours worked in excess of 55½ per week shall be paid for as overtime. (3) The wages to be paid for the ordinary hours of work shall be at the rate of 5½d. (11 cents) per hour for the time worked. For any overtime—that is, hours worked in excess of the 55½ hours per week—there shall be paid wages at the rate of 6½d. (13 cents) per hour. A corresponding advance shall be given to lads and youths under 21 years of age. Another agreement between the same associations relates to the price to be paid per piece for pressing in hydraulic presses: Under 40 yds. of 37 ins. in length, 5d. (10 cts.) per piece; 40 yds. of 37 ins. and under 50 yds. 6d. (12 cts.) per piece; 50 yds. of 37 ins. to 67 yds. of 36 ins. 7d. (14 cts.) per piece; and for every yard of 36 ins. above 67 yds., 1 halfpenny (1 ct.) per yard extra. It is also provided that in pressing patterns the gross yards pressed per week shall be paid for in accordance with the piece scale.

According to a British Board of Trade report the total known coal production of the world (exclusive of brown coal or lignite) in 1911 was about 1,050,000,000 tons, of which the United Kingdom produced more than one-fourth and the United States more than two-fifths. As compared with population the production in the United Kingdom surpasses that in the United States, the amount being 6 tons per head, as against under 5 tons per head. The output in the five principal coal-producing countries in 1911 was as follows: United Kingdom, 271,899,000 tons; Germany, 158,164,000 (provisional figures); France, 38,023,000 (provisional figures); Belgium, 22,683,000; and the United States, 443,025,000 (privisional figures). In the United Kingdom, Germany and France the production in 1911 exceeded that of any previous year.

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HARRY McCORMACK, Editor.

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NOTES AND COMMENTS.

New Armor Plate Process.

Sheffield steel experts are awaiting with considerable interest further information concerning tests which, it is stated, have been applied with some success to armor plates manufactured by a new process which, the inventor claims, renders them capable of resisting projectiles of the highest power.

The inventor is William Henry Worrall, of Sheffield. He states that the new armor plate does not at all rely upon any new ingredient for its increased resisting power, but that this is obtained as the result of a different process of hardening, largely secured by the welding or bonding of four or six sheets of metal into one plate, instead of molding the plate as a whole in one ingot. The main object is to effect a thorough homogeneous hardness. This, it is said, will permit of iron clads being as efficiently protected with much thinner and lighter plates than is at present the case.

Several experts express some doubt as to whether the welding of a number of plates contributes to greater homogeneity. They all agree that experiments conducted on somewhat similar lines have not hitherto been attended with success. Dr. J. O. Arnold, F. R. S., professor of metallurgy at Sheffield University, said:

Practical experience in armor plate manufacture is that you must have the face sufficiently hard and with a sufficient depth of hardness to smash up a shell. No reliable estimate can be formed of the value of a plate until it has been drastically tested by the Admiralty under standard conditions. So far as I know, there is only one plate of this so-called bonded process of manufacture which has been so tested, and that was a failure. There is a new system of manufacturing armor plates, at present in the experimental stage, which consists of welding a face of high-speed steel on to the relative soft backing of the plate. This has been done with some measure of success, but the ultimate value of the plate can only be determined by an Admiralty test. I see it is claimed that Mr. Worrall's plate has withstood a 14-inch shell. If that is so, it must have been an Admiralty test, because I do not think any private firms are equipped with such a gun. The cost of this alone would be about $150,000, and the shell would cost $600. In the absence of further information as to the process and the nature and conditions of the test, I prefer to offer no more definite opinion as to the value of the invention.

Practical Research.

The Metal Industry publishes an editorial commenting on the type of research paper commonly published and cites some lines of research upon which the metal industries are very desirous of research work being done. We quote from their editorial:

One of the principal objections to the scientific papers read before scientific societies nowadays is that they are of no value to the practical man. While such papers may be of much scientific interest to purely scientific societies, technical societies, by which we mean societies consisting of scientists and manufacturers, require a different style of paper. We propose to point out a few lines of research which require elucidation from the manufacturer's point of view. Many statements have been published at different times which are quite in variance to facts obtained in practice. We shall shortly publish an article on the use of arsenical copper for making brass sheets by cold rolling, which are the results of practical experiments on the large scale and which give quite a different version to the generally accepted theories.

A point which needs elucidating is the effect of 1 or 2 per cent antimony on gun metal. Many hundreds of tons of gun metal made from scrap are sold containing about 10 per cent of the tin replaced by antimony. Engineers do not mind it so long as the requisite strength can be obtained. What is wanted is a series of experiments on the manufacturing scale made on various gun metal mixtures using pure metals, with the addition of nil, 0.5, 1, 1½, and 2 per cent, etc., of antimony in place of the tin, testing the tensile strength and elongation. The same series could be repeated with arsenical copper. Every practical brass founder knows he can get a better average tensile and elongation with arsenical copper than with electrolytic copper. No one has yet suggested a satisfactory reason why it is so. The arsenic may act as a deoxidiser or it may act as a toughener, perhaps both.

If 2 per cent of the expensive metal tin can be replaced by the cheaper metal antimony in good quality

gun metals, it means a substantial saving in money, especially as the antimony does not appear to be detrimental and it only wants experiments on the manufacturing scale to prove it, say 100 pounds of alloy. The maximum amount of zinc to be added to ordinary gun metal without serious loss of strength would be valuable to engineers, as would also the minimum amount which would give sound castings. The effect of lead on the tensile of gun metal would be interesting. To get the best practical results from microscopy a standard series of photographs of different alloys cast on the manufacturing scale would be a boon to practical metallurgists. At the present time everyone must prepare his own standards, but if a series were published, just giving the mixture and whether it was good, burnt, cast too hot or too cold, he would merely have to polish his section, etch it, look up the alloy nearest to his sample and see at once if it is burnt or whatever may be the matter with it. Nearly all published micrographs are for the expert's use, and not for the practical man.

Some interesting statistics from the Amazon Basin, via Para, during September and October of 1912 are published by the Board of Trade Journal, from the British acting consul at Para. The districts referred to include Para, Manaos, Iquitos, and Itacoatiara, and the previous year's figures are appended for the purpose of comparison. The total exports during September amounted to some 2,511,100 kilos (kilo = 2.2 pounds), of which 1,241,600 kilos went to the United States and 1,269,500 kilos to Europe. Of the total amount, 1,367,600 kilos were comprised of fine rubber, 243,100 kilos of medium, 597,300 kilos of coarse, and 303,100 kilos of caucho. A comparison with the corresponding month of 1911 shows a decrease in the total amount exported of about 541,600 kilos, which is solely accounted for in the figures relating to the United States, for whereas in 1911 the September exports to that country amounted to 2,043,600 kilos, they declined in 1912 to 1,241,600 kilos, or a drop of some 802,000 kilos. The European figures, on the other hand, show a considerable improvement at 1,269,500 kilos, against 1,009,100 kilos for the corresponding period of 1911. With regard to the month of October, a remarkable expansion is noticeable, and the total exports at 4,097,100 kilos show an advance of about 1,586,000 kilos over the preceding month's figures and 1,756,700 kilos over those for October, 1911. The United States imports were during this month increased as compared with the 1911 figures by about 1,248,000 kilos and the European imports by some 508,800 kilos. Of the total October exports, 2,442,200 kilos were of fine grade, 355,000 kilos medium, 810,100 kilos coarse, and 489,800 kilos caucho. It will be noticed from the above figures that whereas the exports for the two months under consideration in 1911 totaled 5,393,100 kilos, the 1912 figure stands at 6,608,200 kilos, or an increase of 1,215,100 kilos.

BRAYSHAW ON HARDENING TOOL STEELS

In each of the last three issues of the Engineering Magazine for 1912 Shipley N. Brayshaw, of Manchester, England, presented papers on "The Hardening of Carbon and Low-Tungsten Tool Steels." The material was originally read before the Institution of Mechanical Engineers, in 1910, and re-written for the publication just mentioned. Of course, the essential data remained unchanged, although more presentably arranged at its second appearance.

The experimental work extended over many months, necessitating using several lots of material, but always adhering to only two carefully specified types of commercial tool steel. One was a 1.15% carbon steel; the other as similar as possible in composition but containing .5% tungsten.

The investigations comprised determinations of the heating and cooling curves, hardening at various temperatures, the influence of the maximum temperature and the rate of cooling on the recalescence, bending tests, change in length due to quenching from various temperatures, effect of quenching in water and in oil, effect of various preliminary temperatures on the hardening property, change in length due to annealing, the effect of tempering on the bending tests and the tensile test as influenced by hardening and tempering.

The paper is largely a record of experiments; the Brayshaw salt-bath furnace in which the samples were heated to closely regulated temperatures is mentioned; the bending and tensile tests were carried out with the assistance of Sir Robert A. Hadfield in the most approved manner.

Especially noteworthy is the success attained with the Brayshaw furnace. This allowed of accurate temperature regulation and maintenance to within a very few degrees with results sharply defined. In this respect it has set a standard of excellence for all subsequent investigation. The essential part of the furnace is a bath of fused salt, heated to the required temperature, into which the specimens are lowered and in which they soak until they have acquired the desired temperature or remained any desired length of time. Adequate stirring of the bath equalizes the temperature and allows its easy determination by standard pyrometers.

The hardening temperature of the low-tungsten steel was found to be 738°C. The phenomenon is discussed at length although only confirming previous results.

The recalescence is then discussed and shown to be influenced by several conditions.

Oven a hundred bending tests were carried out by Sir Robert A. Hadfield on each of the two types of steel which Brayshaw prepared and heat treated. An interesting result was obtained when the low-tungsten steel was heated to just below the hardening temperature and quenched in oil; this gave an elastic limit practically twice as high as when quenched in water from the same temperature. Another series of tests

showed that while bars heated above the hardening temperature and quenched in brine varied extremely in their elastic limits, quenching in oil from the same temperatures gave closely uniform results of medium value.

Preliminary annealing at various temperatures proved to have considerable influence on the result of hardening while hard and tough bars were produced by heating well above the hardening temperature in one furnace, soaking briefly just below the hardening temperature in another furnace and then quenching in brine. The specific temperatures and soaking periods for this two-furnace treatment which should produce bars neither longer nor shorter after hardening were accurately ascertained.

Tempering the low-tungsten bars raised the elastic limit by half without seriously impairing the hardness. Tensile tests on both the low-tungsten and carbon bars gave similar results; tempering at 250 to 300° raising the ultimate strength nearly twice and the elastic limit full 4 times. Thus low-tungsten bars which had an elastic limit of about 14 tons per sq. in. and a maximum stress of 74 tons per sq. in. after hardening had their elastic limit raised to about 56 tons and stress raised to 114 tons with hardness lowered only from 102 to 85, scleroscope test.

The research is certainly a valuable contribution to the metallurgy of steel; it was well carried out and of great practical significance. The lack of microscopic examination and structural correlation is highly conspicuous. Such an examination of each of the specimens would strongly tend to unite and systematize the results otherwise unconnected and unexplained.

H. B. PULSIFER.

THE SECOND ANNUAL REPORT OF THE DIRECTOR OF THE BUREAU OF MINES.

This report requires some 88 pages to present the history, present activities and future plans of this new division of the government service. The report covers the fiscal year ending June 30, 1912.

Director Joseph A. Holmes evidently has his work well in hand and is able to justify the existence of the bureau so strongly that further discussion from those who have seen no field for its usefulness would appear quite out of order. At the same time we do not observe that the work has in any way usurped the activities of independent engineers.

As in the previous year, the appropriation from Congress provided for scarcely more than continuation of the mine rescue and fuel investigation work taken over from the Geological Survey when the bureau was authorized. Of the $475,000 available, over $300,000 went to investigating mine accidents and over $100,000 to testing fuels; general expenses amounted to $54,000.

The abstracted Table I indicates the satisfactory tendency as regards the coal mine accidents:

TABLE I.

			Number killed			
Year.	Production, short tons.	Employed.	Total.	Per 1,000.	Per million tons.	Tons per death.
1907.....	461,406,000	665,418	3,197	4.88	6.93	144,000
1908.....	404,933,000	672,794	2,449	3.64	6.05	165,000
1909.....	460,761,000	666,523	2,668	4.00	5.79	173,000
1910.....	501,596,000	725,030	2,840	3.92	5.66	177,000
1911.....	496,221,000	728,348	2,719	3.72	5.48	183,000

A considerable part of the fuel investigation related directly to the coal purchased on specification by the various branches of the government and positively effected saving of many thousand dollars as well as insuring specified fuel for government power plants, public buildings and naval stations.

A peculiarity of the organization is that a large part of that work which we would properly call chemical engineering is cared for by the mechanical division, under charge of a mechanical engineer; inspection of fuel, testing fuel, prevention of smoke, special tests of lignite and peat, combustion in gas producers, the use of electricity in metallurgy are some of the instances mentioned. The chemical division appears rather related to chemical analysis. Original investigation by the chemists is, however, not entirely suppressed along the line of fuel investigation and mineral conservation.

Conspicuous features of the year's work are mentioned under the headings of Mine-Accidents Investigations, Mine-Rescue Cars and Stations, Mine-Safety Demonstration and Fuel Investigations.

The needs of the bureau are enumerated under each of the activities now going on or planned; grounds, buildings and equipment are needed for present work under way and the field of the metal mines and general mineral conservation cannot be more than superficially inspected.

Accidents in metal mines are almost as frequent as in the coal mines, various metallurgical works have unhealthful environments and the general waste in mines, mills and smelters is enormous.

Preliminary smelter-fume investigation is being undertaken by Chief Physical Chemist Cottrell and the same is being done for several mineral industries by Mineral Chemist Parsons. A minor problem of the reduction of iron ores by oil is being solved by D. A. Lyon; losses in zinc mining and milling in the Joplin district have been studied by C. A. Wright; titaniferous iron ores in New York and Wyoming have been studied by J. T. Singewald, Jr.; tunneling methods by D. W. Brunton; utilization of mica and feldspar by A. S. Watts and the rare and radium minerals will be studied by R. B. Moore and assistants at Denver.

Special mining reports for the general public are in progress of preparation by Dwight E. Woodbridge and by Brunton and Davis; metallurgical reports of the same general nature are under way by Birkinbine, Fulton and by Sharwood, T. R. Woodbridge and J. A. Davis.

As might be expected, the major part of the report concerns coal mines and fuels. A special investiga-

tion of European coal mines was made by Chief Mining Engineer Rice and a party of commercial engineers. Gas explosions, dust explosions and accidents from handling explosives, accidents from electricity and mine lights were studied. Ventilation, fires and refuge chambers received attention. Credit is given to the engineers supervising or carrying out all this work. The mine-rescue work requires several pages for detailed exposition; then an account is given of the work done studying the chemical nature of mine and natural gas; there is a long record of the work done on explosives, electrical details and the corrosion of iron and steel in mine equipment.

The fuel investigations as enumerated comprise statements of the amount and value of the coal purchased for the government, its inspection and testing; investigations of gas-producers, briquetting machines, coking, the origin and use of lignite and peat, the chemical and microscopical structure of coal, the storage of coal, the technology of petroleum and gas.

At the close of the report is a list of publications issued during the year and other details of administrative nature. H. B. PULSIFER.

The English Textilose Manufacturing Co. has erected large works in Trafford Park, Manchester, England, for the production of textilose, the new jute substitute. The Manchester Guardian stated in a recent issue: "Textilose appears to have succeeded in more thoroughly attracting expert attention than any other jute substitute yet put forward. The Austrian rights of making the new product, which is manufactured from paper yarn and cotton waste by a patented process, were acquired some time ago by the Austrian Jute Cartel, which is erecting a plant. A license has also been granted to a Belgian firm, while a commission appointed by the German Jute Cartel is now engaged in investigating the merits of textilose with a view to purchasing the German patent rights. It has been reported that a plant is to be built in Spain, capable of turning out 12,000 kilos (26,455 lbs.) of textilose yarn per day, and that an international syndicate is negotiating for the patent rights in all countries where they have not already been disposed of.

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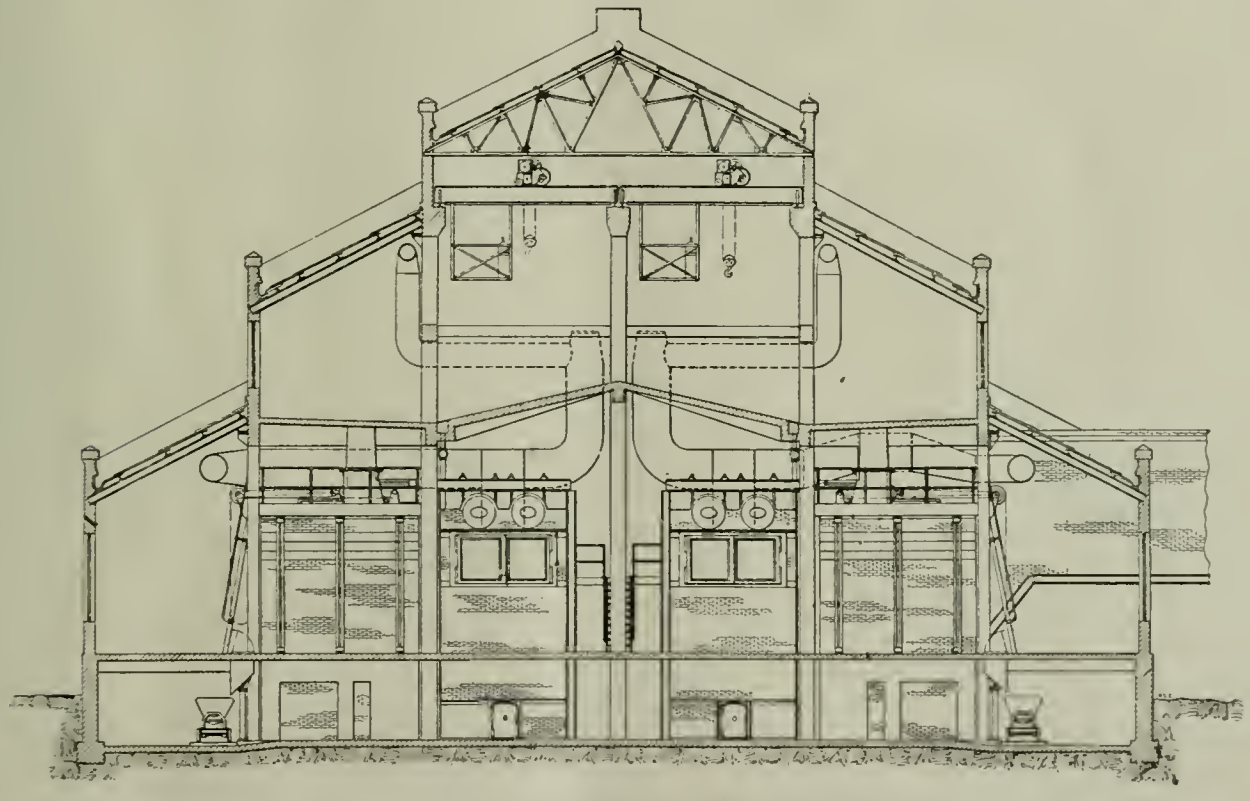
THE REFUSE DISPOSAL PLANT OF MILWAUKEE, WIS.

By FRANK C. PERKINS.

The economical and sanitary disposal of city garbage, rubbish and other city refuse is of the utmost importance, and the solution of this problem by the Milwaukee municipal administration is of special interest. The refuse destructor plant recently completed by the Board of Public Works of the city of Milwaukee, Wis., consists of four separate independent units each having a capacity of 75 tons per day, giving a daily capacity for the complete plant of 300 tons. Resident Engineer Samuel A. Greeley gives the revenue from the steam produced per ton of refuse incinerated as $1.072 at the contract price of 4 cents per 100 lbs. for 2,680 lbs. of steam, the gross cost per ton being $.407, giving a net profit of $.665 per ton. In the test giving these results, 126.81 tons of refuse were consumed in 37 hours, the rate of burning being 64 lbs. per square foot area of destructor, with 1.34 lbs. of steam evaporated from and at 212° F. per pound of refuse destroyed. The temperature of the combustion chamber averaged 1,664° F., and the minimum temperature was 1,267° F., while the temperature of the air supply was 351° F.



Section of Refuse Disposal Plant at Milwaukee, Wis.

The gross cost per ton above mentioned includes labor, steam and electricity utilized and complete cost of operation.

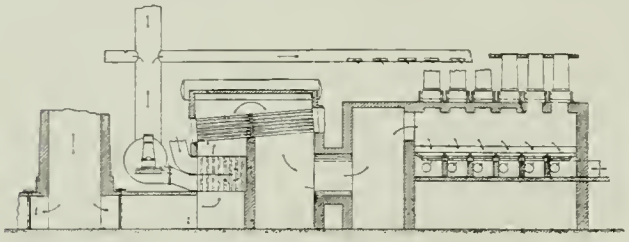
The Milwaukee destructor plant is installed in a rectangular brick building having two stories and a basement, one of the four 75-ton refuse destructor units of the Heenan type being arranged in each corner. The electrical machinery, recording instruments and auxiliary apparatus, are located on the ground floor level, where the principal work of clinkering and operating the plant is accomplished, while the

basement is used for furnace cleaning and the clinker railway and the upper story for the storage of refuse and feeding floor.

Electrically operated cranes are used for hoisting the refuse into the building and distributing the same into the various storage bins, from which it is fed to the furnaces, the men raking or shoveling the material into the mouths of the containers or rectangular steel chutes.

There are two classes of carts used for collecting the city refuse and garbage, the rubbish being received at the plant in 2-horse wagons of 2½ cu. yds. capacity of the bottom dumping type, while the garbage is handled in 1-horse carts of 1½ cu. yds. capacity having removable steel bodies which are hoisted by the electric cranes and dumped into the bins on the feeding floor.

The sliding doors forming the furnace openings serve as the bottoms of the containers or rectangular steel chutes which receive the rubbish, ashes and garbage. These containers are kept charged with the



Method of Ventilation.

mixed material at all times, and the firemen from the floor below control the doors which allow the contents of the chutes to pass into the furnace.

This mixture of garbage and refuse falls onto a drying hearth, where a large part of the moisture is taken up by the hot gases and carried away, after which the dried material is raked forward on the grate by the firemen, small stoking doors being provided for this purpose. As soon as a thick body of clinker has been formed it is broken up by bars and is drawn out of the furnace through the large counterweighted clinkering doors. The clinker passes through holes in the floor into steel dump cars on the clinker railway in the basement below, when it is moved outside the building to the cooling yards.

There are six separate grates provided for each furnace, three of which are located on each side of a central combustion chamber through which the products of combustion of all six grates pass and are thoroughly mixed, the velocity through this combustion chamber being very slow. The gases, after leaving the combustion chambers, pass over the heating surface of 200 H. P. water tubular boilers, one for each unit. The gases then pass through an air heater or regenerator and out of the chimney, the combustion being controlled by force draft entirely. An engine driven fan is utilized for drawing the air from ventilating ducts in the building, an air heater raising the temperature to about 300°.

It is stated that several times the cubic contents of the building are required per hour for combustion purposes when the plant is in full operation, so that every few minutes the air in the building is completely renewed, thus preventing the escape of any gases from the building except through the furnaces and out of the chimney. This is a most sanitary system, as it is claimed fresh air thus enters the building, insuring a complete renewal of all the air every 8 minutes.

There are controlling valves provided for the separate ash pits under each grate, in order that the rate of combustion and the amount of air supplied may be changed as desired under the various grates. There is a separate fan and engine installed with independent flows for each unit. This plant has been in most successful operation for several months, disposing of all the garbage rubbish and refuse with economy and in a most sanitary manner.

According to information obtained from reliable sources, the following are the average wages paid to persons employed in the metal-working industries in Berlin: Per hour—operator of lathe, 14 to 18 cts.; operator of drill press, 11 to 13 cts.; operator of milling machine, 13 to 14 cts.; operator of planer, 14 to 17 cts.; operator of grinder, 14 to 15 cts.; laborers, 11 to 13c. Per week—inspectors, $11 to $18; tool makers, $18 to $21; blacksmiths and polishers, $14 to $17. Per month—foremen, $54 to $62; watchmen, $24 to $29; shop clerks, $21 to $33; bookkeepers, $29 to $41; draftsmen, $43 to $54. Each of the employes enumerated above usually works for nine hours daily, regardless of whether he is paid by the hour, week or month. Piece workers receive considerably higher wages than those who work by the hour or week. Thus, lathe operators who do piece work may receive a maximum of 23 cts. per hour; drill-press operators, 19 cts.; milling machine operators, 19 cts.; planer operators, 20 cts.; blacksmiths, 20 cts., and polishers, 19 cts. The average cost to large consumers of machine steel in round bars ½ in. to 2½ ins. in diameter is $4.16 per 100 kilos (1.89 cts. per pound); carbon tool steel of the same dimensions ranges from 21 to 43 cts. per kilo (9.53 to 19.5 cts. per pound); while the price per kilo (2.2 lbs.) of high-speed steel is from $1.07 to $2.02 (48.5 to 91.6 cts. per pound).

Swiss cholocate exports last year were 15 million pounds, against 12½ million pounds in 1911 and 10 4/5 million pounds in 1910.

Swedish iron-ore exports in 1912 were 5,522,746 metric tons, against 5,106,764 tons in 1911 and 4,434,781 tons in 1910.

MANUFACTURE OF RAW SUGAR IN THE PHILIPPINE AND HAWAIIAN ISLANDS.*

By C. A. BROWNE.†

It was my pleasure a year ago to address the students of this course upon the chemistry of raw-sugar production. That paper was published in the School of Mines Quarterly, of April, 1911, and to save time and prevent repetition I will simply refer you to it for a description of the cane and beet sugar industry, and for statistcis upon sugar in general. As a subject for this year, it occurred to me that a brief account of the methods of producing sugar in some of our colonial possessions would be of interest. I have therefore selected the Philippine Islands, where agricultural and technical methods are still very primitive, and the Hawaiian Islands, where the processes are among the best in the world.

The sugar from the Hawaiian Islands and the Philippines is mostly exported to the United States, where it is refined. A great deal of the Hawaiian sugar is shipped to San Francisco, the nearest American port; the rest of it comes to the eastern ports, principally Philadelphia, by way of the Isthmus of Tehuantepec, where it is transported in trains across Mexico to the Gulf, and reshipped. The Philippine sugar is shipped mostly to New York and comes, for the most part, by way of the Suez canal and the Mediterranean, an occasional shipload coming by way of Panama or around Cape Horn.

The cane producing countries are situated, for the most part, each side of the equator between the Tropics of Cancer and Capricorn. At one time the cane grew only in India, from which country its cultivation spread eastward and westward. Ancient Chinese writings mentioned the introduction of cane into China several centuries B. C.; its cultivation was extended eastward by the Malayan and Polynesian tribes to the East Indies, the Philippines, the Pacific Islands, and finally to Hawaii, where it was found growing when these islands were discovered.

SUGAR PRODUCTION IN THE PHILIPPINES.

We will now look first at the agricultural side of the Philippine sugar industry. The beast of burden used almost wholly in the Philippines is the caraboo, a kind of native ox, very savage in the wild state, but easily domesticated. The plows are made of wood and are of very primitive workmanship.

After the ground is prepared, parallel furrows are plowed across the fields and into these furrows the cane tops, which serve as seed, are planted.

After the cane tops are planted and covered with earth, the buds quickly germinate and the young cane plants soon appear above the ground. The crop is cultivated by plowing and hoeing until the rainy season begins, when the cane is left until the time of harvest, which is usually 9 to 14 months from the time of planting.

When the sugar cane is harvested, the ground is not usually replowed, but the old stubble is left, from the underground buds of which a second crop of cane, known as stubble or "ratoon" cane, is produced. In the Philippines, from two to eight ratoon crops are taken off before the land is plowed up and replanted. Ratooning saves the labor and expense of planting, but the continuous growing of the same crop year after year without replowing is a heavy drain upon the fertility of the land; long ratooning, for this reason, is not followed in the most progressive countries.

The harvesting of sugar cane is done by hand in all countries. Inventors have spent years and fortunes in trying to perfect machines which would cut the cane stalks close to the ground, strip them of their leaves and tops and gather them into bundles, after the plan of the wheat harvester. They have not as yet succeeded. A sugar cane field at the time of harvest is almost a jungle; stalks are interwined and blown down by the wind so that the cutting and trimming of each cane is a separate problem, for which hand labor seems to be the only solution.

The green tops of the canes, containing the leaves and buds, are of no use for making sugar, but are exceedingly valuable as seed. The tops are saved and the leaves removed by husking, much in the same way as ears of corn are husked. This part of the work is done by women and children.

After the stalks of cane have been cut and loaded upon wagons, they are hauled to the factory and unloaded preparatory to the grinding.

The grinding of sugar cane in the Philippines is performed in some places by antiquated steam engines and in some places by the still more primitive method of using oxen. In an ox-driven mill the two animals are attached to sweeps upon opposite sides; the sweeps are connected with a vertical shaft which operates the rollers of the mill by means of a bevel gear. The cane juice escapes from the mill through a small gutter and flows to the evaporator, where it is boiled into sugar. The extractive power of these mills is very low, and usually less than ¾ of the sugar in the cane is expressed. The pressed cane, or bagasse, constitutes the principal supply of fuel, but as it contains a large amount of unexpressed juice, it must first be dried before it can be burned. The drying is carried out by spreading in the sun in open yards.

The evaporation of the juice in the Philippines is carried out in open pans or kettles which are set in large fire-places, heated by burning bagasse. The juice from the mill is first strained through a screen, to remove suspended impurities, into the first pan of the evaporator. The pans are usually arranged in two series of five, which open into one another at the top; each succeeding pan as shown in the photograph is slightly smaller in size, but higher in elevation, the

*From a special lecture in the Department of Chemistry, Columbia University, and reprinted in the School of Mines Quarterly.

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arrangement being step-like in appearance. In the first pan the juice is warmed to 70 or 80° C.; a little lime is added and the coagulated impurities skimmed off into scum tanks which are placed at an elevation upon one side. The common utensil for skimming and ladling is an old kerosene can, attached to a pole. It is interesting to know that the kerosene can in some parts of the Philippines is the standard measure of volume.

The hot juice is ladled from the first into the second pan of the evaporator, the general plan being always to keep the smaller pans full, so that scums, when boiling over, will discharge backwards into the preceding vessel. More lime is also added, usually half a cocoanut shell full at a time, according to the judgment of the sugar maker. The plan is to keep the juice always slightly acid; the sugar maker relies for this upon color, smell and taste, the use of litmus or other indicator being generally unknown.

As the juice is ladled from pan to pan it becomes more and more concentrated and in the last pan becomes sufficiently thick to crystallize. When this point is reached, as is determined by taking out a sample of the product upon a stick, the contents of the pan are ladled onto wooden trays and shoveled with a spade until the mass sets to a thick material resembling concrete. The crystallization, which is attended by the liberation of considerable heat, requires from 15 min. to an hour, according to the grade of sugar. The sugar made in this way contains, of course, all the impurities of the juice except those removed by the scums. There is consequently no molasses as in processes wherein the sugar is purged. The concrete is then ground up and packed in wicker mats holding about 50 pounds.

Most of the sugar made by this method of manufacture is classified by color into grades. The lightest, or first grade, polarizes about 88°; the second grade polarizes about 86°; the third grade polarizes from 82 to 84°; a fourth, very dark grade of mat sugar polarizing 80° or below is also marketed occasionally. The darkening in color of the product is due either to over liming or to burning in the kettles; there is a curious belief among natives that boiling the sugar at night will cause the sugar to become tinged with darkness, thus lowering its grade.

The sugar after leaving the factory is transported by small boats to Iloilo or Manila, where it is stored for shipment to this country. Sugar which has been damaged by water from leaky boats or by rain is spread out upon trays to dry in the sun.

Only about 55 per cent of the sucrose in the cane is obtained as raw sugar by the primitive methods of manufacture carried on in the Philippines; 25 per cent of the sugar is lost in the bagasse; the remaining 20 per cent represents the loss in the scums, and the sugar destroyed by inversion, caramelization, and in other ways. Attempts are being made at present by the Philippine authorities to improve the methods of sugar manufacture. Herbert Walker, a young chemist, spent many months visiting the plantations of the island of Negros, carrying with him a polariscope and other apparatus, studying methods of sugar manufacture, and wherever possible suggesting methods of improvement. As an indication of what the new order of things is destined to accomplish, it is worth mentioning that on Feb. 21, 1912, a modern sugar factory equipped with the latest machinery, mills, evaporators, vacuum pans, centrifugals, and crystallizers, began its operation. The first output of this factory was a sugar polarizing 98.2°, the highest grade of plantation sugar manufactured in the Philippines up to that time. Other central sugar factories are being erected, and it may be stated with confidence that in those islands, where the sugar content of the juices reaches over 18 per cent, with a purity exceeding 90 per cent, the future outlook is most promising.

SUGAR PRODUCTION IN THE HAWAIIAN ISLANDS.

Passing now to our other possession in the Pacific, the Hawaiian Islands, we shall see what the sugar industry in the Philippines must aspire to. Fifty years ago the methods of cultivation and manufacture were as primitive as those just noted in the Philippines. With the establishment of reciprocity with the Hawaiian Islands in 1875, by which Hawaiian sugar was admitted into the United States free of duty, a great impetus was given to the industry by the influx of American capital. This impetus was still more intensified by the annexation of the islands to the United States in 1898.

Sugar cane thrives most luxuriantly in the Hawaiian Islands and the growth of cane is also promoted by superior methods of cultivation and irrigation. A yield of 12 tons of sugar per acre of land has been obtained, whereas 50 years ago not more than one ton of sugar could be obtained from that area. The production of sugar per acre will probably average about four times as much as in the Philippines, although if we figure the ratio per acre per year, the proportion will be reduced nearly one-half.

Sugar cane is cultivated in the Hawaiian Islands for the most part upon table lands which slope downward towards the coast. The factories, for convenience in shipping and receiving supplies, are usually situated near the coast, very often upon high headlands.

The land is prepared for the cane crop in Hawaii by means of large plows which are drawn by engines and cables across the field. The plow turns four furrows at one operation, and is reversible; the plow beam carries eight shares, only four of which are in operation at one time, the remaining four being elevated. The plow is drawn by a cable stretched between drums upon two traction engines on opposite sides of the field; the plow is drawn back and forth between the two engines, the beam being tilted one side down in one direction, and the other side down in the other. The plowing in the Philippines may be more pic-

turesque than this, but as regards efficiency and economy of labor there is no comparison between the two.

Much of the work done in the cane fields of the Hawaiian Islands is performed by labor-saving devices of a high order. A great deal of the work must however be done by hand; the planting of the cane is all hand work, so also the husking of the cane tops for seed by native and Japanese labor.

After planting the tops and covering with earth, the cane fields are usually irrigated, and as the young cane begins to develop, cultivation is resorted to, very much as in the large corn fields of our Western states. "Ratooning" is never carried beyond one year; the field is then replowed for a new crop of cane.

The sugar cane in the Hawaiian Islands is usually allowed to reach its maximum development, and the crop is frequently not harvested until 22 months after planting. This long period of growth, nearly two years, favors, of course, a large crop of cane, but the return of sugar per acre, to be compared with countries which cut the cane yearly, must of course be divided by two.

The cane stalks are cut and trimmed by hand and then transported to the factory which is frequently many miles distant. A most ingenious method of transporting cane in some of the Hawaiian Islands is by means of flumes, which, starting as open troughs in the upper cane fields, are carried down to join other sluiceways until there is finally a small river of water carrying with it a tangled mass of cane stalks. The cane as fast as cut is carried to the nearest sluice, where it is thrown, stalk by stalk, into the running water. Owing to the liability of the stalks to become entangled in the flumes and thus stop the movement of the cane, the waterways are patrolled by men who keep the sluiceways clear. In some places the flumes span wide ravines several hundred feet in depth.

At the ending of a flume at the sugar factory, the cane stalks are discharged from above into railroad cars, the excess of water escaping through the bottom.

The question is frequently raised whether this long contact of the cane stalks with running water does not wash out a considerable amount of sugar. Mr. Walker informed me that after evaporating many liters of flume water, and applying the very delivate α-naphthol test with H_2SO_4, only the faintest coloration developed, and a calculation to the original volume of flume water showed that the losses from this cause were almost negligible. This is what would be expected. There is of course a very slight loss of sugar from the ruptured cells at the cut ends of the stalk, but nothing can escape from the uninjured tissues. The fluming process really improves the cane, for the water removes adhering dirt and trash which would otherwise find its way into the juice.

The mills for grinding sugar cane in the Hawaiian Islands are the most powerful in the world. This part of the mill, which first receives the cane from the conyerer, is called the crusher; it reduces the cane stalks to an even pulpy blanket of fiber and at the same time removes from 50 to 60 per cent of the juice. The blanket of pulp is next carried between other rollers which are arranged in sets of three, two below and one above. These constitute the mill proper, and according to the degree of extraction desired there are six-roller mills, nine-roller mills, twelve-roller mills, and even fifteen-roller mills, the entire plant being thus made of detachable mills of three rollers each. The extracting power of each mill is increased by powerful hydraulic presses; to increase further the extraction of sugar the blanket of fiber between each two sets of rollers is sprayed with fine jets of water which is delivered from transverse sprinkling pipes shown in the photograph. This water is absorbed by the fiber and being again squeezed out by the next rollers carries with it more of the sugar-containing juice, which is of course considerably diluted by the wetting. The very dilute juice from the last mill is sometimes used instead of water for spraying the fiber from the first mill. This process of wetting and repressing is called "maceration" and it requires careful calculation and good management to know just when the evaporation of the added water begins to cost more than the value of the extra sugar recovered. The cost of fuel, labor, and many other factors, all have to be considered and a system of maceration which is profitable in one country might be ruinous elsewhere. In the Hawaiian Islands 30 per cent or more of water is sprinkled upon the ground cane, and with the large mills which are employed, over 95 per cent and in some cases over 97 per cent of the total sugar in the cane is extracted. These figures, compared with the 70 and 75 per cent extraction obtained in the Philippines, show what possibilities there are for improvement in the latter islands.

The juice, after extraction, is clarified with lime and sulphurous acid, and the impurities of the hot juice removed in powerful filter presses. The clarified juice is then concentrated in vacuum evaporators to a syrup, which is further concentrated in a vacuum pan to a thick mass of crystals.

The graining of the sugar in the vacuum pans, the centrifugal separation of the molasses, and the drying and bagging of the sugar, are carried out essentially as described in the paper already referred to.*

The sugar, after it has been bagged, is conveyed to ships for transportation to the United States. If the factory is located in the interior, the sugar is carried down to the coast by rail or by means of traction engines, which transport many wagon loads of sugar at one haul. If the factory is located upon a headland near the sea, the sugar is run down to the ship upon cables.

COMMERCIAL PROBLEMS OF THE SUGAR TRADE.

The transportation of sugar from the Philippines and Hawaiian Islands, and the marketing of the commodity, present a number of problems in which the

*The Quarterly, April, 1911.

chemist is more or less directly concerned.

There is first the question of deterioration. Moist sugar is very susceptible to fermentation and the fumes from a cargo of sweating sugar after the ship has been in the tropics is almost overpowering. A moist sugar testing 88° at Manila or Iloilo may polarize only 86° when it arrives at its destination, and the owner of the sugar usually lays the blame upon the chemist or the transportation company rather than upon himself. The Hawaiian manufacturers dry their sugar, and their product, as regards deterioration, always arrives in as sound condition as when placed upon ship.

A second question, which is always arising, is the damage to the sugar during shipment. This damage results mostly from wetting and may happen in several ways. The seepage of sea water into the hold of an old freight boat may damage seriously the bags of sugar resting upon the bottom of the ship, especially if the ship owners are too parsimonious to employ dunnage for the protection of the cargo. Damage to sugar by salt water must usually be paid by the owners of the ship, and a chemist is sometimes confronted with the problem of determining whether a given lot of sugar is damaged by salt or by fresh water. The problem is not as easy as it might seem at first sight.

The damage to sugar by fresh water usually results from sweating; in such cases the top bags in the hold usually suffer the damage. The vapors from the lower tiers of warm sugar condense upon the roof of the hold and dropping back, wet the upper sacks of sugar, very much like a shower of rain. If it is all one owner's sugar, it makes, of course, little difference; one part of his sugar has dried out a little and another part has become correspondingly more moist. But when this moisture falls back upon some other owner's sugar, complications arise.

The breaking of bags during transport is also a frequent occurrence. The damage to Hawaiian sugar in transporting across the Isthmus of Tehauntepec is sometimes considerable. Bags are also broken on the ship and at the dock in discharging the cargo. Sugar lost in this way is called loose sugar; as much as possible of it is saved and it is classified as Mexican loose, ship loose, or dock loose, as the case may be. It is not always easy to determine to what owner the loose sugar belongs; it may be apportioned according to the proportionate ownership of the cargo or in other ways, according to agreement. The amount of sugar damaged in shipment varies greatly. Of a cargo of about 100,000 bags of Hawaiian sugar recently tested in our laboratory, there were about 1,000 bags, or 1 per cent, damaged by fresh water; over 300 bags of Mexican loose, and over 100 bags of dock and ship loose sugar. With the opening of the Panama canal, and direct communication between Honolulu and the eastern parts of this country, we may look for a great improvement in certain matters of transportation.

The valuation of a cargo of sugar after it arrives is a most important question. The value of raw cane sugar is determined by means of the polariscope, according to familiar practice. The method of sampling the cargo may, however, be less familiar.

The need for carefully prescribed rules in sampling sugar becomes very evident when we take into account the very frequent variations in composition between sugar in different parts of the bag or mat. The sugar, for example, may contain lumps of higher or lower polarization than the finer part of the product; the sugar may also retain considerable amounts of molasses, sometimes as high as 30 per cent, which drain during transit or storage and form the "foots" at the bottom of the bag. In addition to the differences in composition of sugar within the single bag or mat are the differences in composition between different packages of the same lot.

Sugar is sampled in the same way as fertilizers and many other commodities, by means of a trier. This implement consists of a long pointed rod of steel with a groove or spoon upon one side. A thrust of the trier into the package forces the sugar along its pathway tightly into the bowl of the spoon; the sugar thus adhering, after the trier is withdrawn, is removed by the thumb, or by means of a scraper, into a covered bucket, and the process is continued until a sufficient number of packages have been sampled to constitute a mix; this number may vary according to the size of lot and kind of sugar from one package to several thousand. The practice of the New York Sugar Trade is to mix twice daily, and in no case is a sample to remain unmixed over night.

After the sugar in the bucket has been well mixed the cans which are to be sent to the chemists are filled, sealed and labeled. When the returns of the chemists come in, an average is made and the result taken as the polarization of the sugar for the number of bags and weight of sugar represented in the sample.

Many tricks were once used in the sampling of sugar, and the sampler, by skillful manipulation of his trier and from the knowledge gained by experience, could draw sugar from the dry or wet part of the bag according to the interests of the party for which he was working.

To eliminate so far as possible the errors of personal equation in sampling, the practice of the New York Sugar Trade is for the samplers of buyer and seller to work alternately hour by hour; the one party in the interval of rest exercising a control upon the operations of the other. The tendencies to draw too high and too low from the package are thus counterbalanced and the personal errors equalized. This method seems as good as any that can be devised.

From this very hasty and very superficial review of but a limited part of the sugar industry of the world, you may perhaps have gained some idea of the enormous breadth of the field. Each individual country and each particular phase of the industry presents special problems which are constantly engaging the attention of experts and specialists.

COST OF PRODUCING CUBAN CANE SUGAR.*

By HENRY P. STARRETT.†

In discussing the cost of production of Cuban cane sugar it may be stated at the outset that no statement as to such costs can be absolutely correct as applied to individual mills, differences in cost being as wide among the different mills as for any staple article where producing conditions differ with locality, cost of raw material, labor wage, efficiency of machinery, and character of transportation facilities.

In the modern sugar mill in which machinery of the highest efficiency has been installed, where the location is on or near a good harbor and docking facilities are available, where the mill company owns and operates its own lands and railroad, and which has as its manager a man who has real executive ability coupled with long sugar experience, sugar can be and is produced for 1.25 cts. a pound, this representing the total cost of the product from time of planting the cane to placing the finished product alongside the ship, and the proportional charge for general and administrative expense.

However, the other extreme is reached in the old mills, which are inefficient in themselves and are located at interior points where they are compelled to pay high freight rates on their sugar product and oftentimes an abnormal price for their cane. Many of the older mills do not own or operate the fields from which their cane is produced, whereas other mills own the land and allow "colonos" or cane farmers to operate the fields. In the first instance some of these mills pay as high as 7 arrobas (arroba equals 25.3664 lbs.) of sugar for each 100 arrobas of cane delivered to the mill or its railroad, while in the latter case, where the mill owns the land, the "colono" receives only from 4 to 5 arrobas of sugar for each 100 arrobas of cane. Under the conditions which obtain with the mills of the first instance the maximum of disadvantage is operating against the possible profits of the mill, and there is no doubt about the fact that many of the mills of this type in Cuba produce sugar at a total cost which is well over 2 cts. a pound and close to the zone of "no profits." The production of such mills, however, probably represents a small percentage of the total production of the island.

It is obviously not fair to consider the cost of production as being either that of the highly efficient modern mill or that of the old and inefficient mill, which is poorly situated as regards transportation facilities. Therefore the only possible method of getting at the average cost would be to determine just what the average mill is, how much sugar it produces annually, and the cost of that production. In line with this theory, the following table shows the total annual production of Cuban sugar for the last four years, the number of active mills which produced the sugar, and the average production of each mill (ton equals 2,240 lbs.):

Season.	Total production. tons.	Number active mills.	Average production per mill, tons.
1908- 9	1,513,582	171	8,851
1909-10	1,804,349	174	10,312
1910-11	1,480,217	172	8,606
1911-12	1,874,714	173	10,837

The average production of each mill on the basis of four years' results is therefore 9,651 tons or 67,557 bags (bag equals 320 lbs.). Experienced sugar men assert that, on the basis of several years results, the average mill will grind to at least 90 per cent of its full capacity each year. This being true, the average theoretical capacity of the Cuban sugar mills is therefore 75,000 bags each per year.

These figures are given to serve as a basis in determining, approximately, the total investment in the average sugar estate, including mill, land, railroad, docks, and all equipment and machinery, in order that an estimate may be made as to just what the interest and depreciation charges should be. The cost of the cane and the cost of its manufacture into sugar will be discussed in their order. Sugar engineers have a "rule-of-thumb" method of calculating the entire cost of such a mill and estate, including railroad and docks, by figuring $15 for each bag of production capacity, and experience has proved that this is a conservative and proper estimate of the total investment necessary. On this basis the average mill company in Cuba has an approximate total investment of $1,150,000. The interest charge, at 5 per cent, would therefore be $56,250 per annum and the depreciation on mill, railroad, and equipment would probably be fairly represented by a charge of 5 per cent on $800,000, the approximate cost of the same, or $40,000 per annum. Depreciation in land fertility is now, and will continue to be for several years to come, more than well covered by its increasing value. The remaining items of "general expense" are for administration, insurance, and taxes, and the total for these three items should not exceed $8,000 a year. The total "general expense" in the average mill is therefore $104,250 per annum.

The two important items entering into cost of production are: Cost of producing, harvesting, and transporting the cane, and actual cost of manufacturing sugar. In order to arrive at the proper conclusions in regard to these items, it is necessary to know about how much cane is needed to produce the 9,651 tons of sugar referred to as being the output of the average Cuban mill. Inasmuch as the sugar content in Cuban cane averages about 14 per cent of the whole, and the average mill secures only about 78 per cent of this content in the process of manufacture, the cane necessary to produce the above amount of sugar under these conditions would be 87,736 tons in theory, while 90,000 tons would probably represent the actual requirement.

*From Daily Consular Report.
†Deputy U. S. Consul at Habana.

The consensus of opinion among planters and engineers seems to be that the average production of sugar cane in Cuba is 22 tons per acre, running considerably more than this in new land and favorable localities, and much lower in old and worn-out land. The cost of this cane per acre, including the cost of clearing, fencing, breaking the soil, planting, and cultivation up to the period of harvest (14 to 18 months after planting) is given as being $60 an acre, with an annual charge for cultivation each succeeding year of $14 an acre for a period of about seven years, the life of the average cane field. This makes a total cost for growing and cultivating the cane for the seven years of $144 an acre, or about $20 per acre per year. On the basis of a production of 22 tons of cane per acre and an annual cost of $20 per acre, the cost of producing the cane is therefore about 90 cts per ton. The cost of cutting the cane and loading it on carts is stated to be not over 70 cts. per ton. The cost of hauling cane from the field and loading on railroad car averages 40 cents per ton; and the cost of railroad haul from the fields to the mill, assuming that the mill company owns its own railroad, is about 30 cts. per ton, depending upon length of haul.

As to the mill cost of manufacturing this cane into sugar engineers and experts state that it will generally run from 50 cts. to $1 per ton of cane, while a fair average for all Cuban mills would be about 75 cts. per ton.

The two general items, cost of cane and cost of manufacture, are therefore:

Producing and cultivating 90,000 tons of cane,. at 90 cts. per ton	$ 81,000
Cutting and loading same on carts, at 70 cts. per ton	63,000
Hauling from fields and loading on railroad cars, at 40 cts. per ton	36,000
Railroad cost for hauling to mill, at 30 cts. per ton..	27,000
Mill cost of manufacture, at 75 cts. per ton	67,000
Total	$274,000

To this amount must be added the "general expenses" amounting to $104,250, making a total of $378,750, which figure represents the cost of producing 9,651 tons of raw sugar. Each ton being of 2,240 lbs., the production in pounds is therefore 21,618,240, and the cost per pound is 1.75 cts.

This of course represents the cost at the mill and does not take into account the cost of transporting the product from the mill to the shipping port, for this varies so widely that no fair estimate could be given, some mills being so situated that they are compelled to pay as high as 60 cents a bag for railroad freight from the mill to the seaboard, while for others which are located on the coast and own their own docking facilities and railroad, the shipping cost is low, being not more than 5 cents a bag. As a rough estimate it can be stated, however, that the average transportation cost from mill to seaport probably does not exceed 32 cents per bag, or an equivalent per pound of 0.1 cents. This would make the total average cost of sugar at seaboard 1.85 cents per pound.

In conclusion it should be reiterated that these figures are only average results, and that this average will be higher or lower according to the season and conditions—that is, whether a large or a small crop of cane is harvested; high or low percentage of sugar content in the cane; and the rise or fall in the wage scale.

THE MICROSCOPICAL EXAMINATION OF VEGETABLE PRODUCTS AS AN ADJUNCT TO THEIR CHEMICAL ANALYSIS.*

By A. L. WINTON.†

In solving the problems of man and nature the analytical chemist too often limits himself to chemical or physico-chemical methods. He is an analytical chemist in the strict sense of the word and not an analyst, which implies a man of broader training and experience, utilizing the principles of other sciences as means to his end. He turns his back on the methods of vegetable and animal histology, physiology and bacteriology, asserting with satisfaction that he is a specialist and as such must limit his field of activity.

This attitude of the analytical chemist may be traced to a misapprehension as to the province of a specialist. Such a worker must be limited only in the field of application and not in training or the methods employed. An oculist, for example, limits himself to defects of vision and diseases of the eye and allied organs, but in order to properly carry out the work of his specialty he must have broad medical training and be conversant with the general principles of optics, bacteriology, chemistry and perhaps other sciences. Specialists in other sciences, both pure and applied, must also have good general training if they are to achieve distinction in their limited fields; otherwise they are in much the same position as the mechanic who, instead of mastering his trade, learns to operate one machine, thus becoming a mere automaton.

Botany and chemistry are generally considered incompatibles. The student of chemistry sometimes takes up bacteriology as a minor subject, but comparatively seldom studies advanced botany, even though he intends to specialize in food analysis, textile chemistry, paper technology or some other subject dealing chiefly with materials of vegetable origin. No physiological chemist would think of pursuing his investigation of animal materials without a working knowledge of animal anatomy, yet agricultural and food analysts and others dealing with vegetable materials too often limit themselves to a knowledge of chemical constituents, ignoring the relation of composition to histological structure.

This is most remarkable, since the methods of vegetable histology, as well as of chemistry, are invalua-

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ble in solving problems relating to the nature or constituents of foods, drugs, fibres and other products of vegetable origin. Sometimes one line of investigation alone is useful, sometimes the other, but often each throws some light on the subject, and the corroboratory results obtained by such widely differing means furnish an indisputable chain of evidence.

Let us look more closely into the nature and relation of these two applied analytical sciences.

Chemical analysis deals with chemical constituents; microscopical analysis deals largely with the form of some of these constituents. Chemical analysis determines the amount of fibre, starch, protein, oil, etc.; microscopical analysis determines the shape, size and other characteristics of the cells and cell contents. Chemical analysis usually stops with the mere determination of the amount of chemical constituents; microscopical analysis goes further and names the particular product from which they were derived. Chemical analysis answers a question only in scientific terms; microscopical analysis, in terms which all can understand.

In many cases, the best idea of a material is gained by following out both lines of investigation. By chemical analysis we learn the percentage of protein, fiber, starch, etc., but not the ingredients from which they were derived; by microscopical analysis we learn the ingredients, but usually gain only an approximate idea of their proportion. Given the results of both analyses, we may often calculate with some exactness the percentage of the different materials present.

If, for example, we find in a sample of wheat bran 11 instead of 16 per cent of protein, and 15 instead of 8 per cent of fiber, we know it is not pure bran, but we do not know the adulterant; if we find corn-cob tissues under the microscope, we learn the adulterant, but not the amount. Knowing that the material is a mixture of bran and ground corn-cob, and knowing the average percentage of protein and fiber in both, we are in a positon to caluclate from the results of the chemical analysis the relative amounts of these ingredients.

Again, if we find in ground mace 40 per cent instead of 20 per cent of fixed oil, we know it is not pure mace; if we find under the microscope a large amount of tissues of the Bombay mace, a material worthless as a spice containing about 60 per cent of fixed oil, we learn the adulterant. Knowing all this, and knowing the average percentage of oil in true mace and Bombay mace, we have the data for calculating roughly the percentage of each in the mixture.

Still again, if in a textile fabric we find a certain percentage of organic fiber insoluble in boiling alkali, we know that the fabric is not all wool. If under the microscope we identify this insoluble fiber as cotton, we have found the missing link in the chain of evidence.

In the analysis of complicated mixtures, we must often rely entirely on microscopical examination. For example, chemical analysis of a mixture of wheat, buckwheat and corn flours gives us little information, and it is only after the characteristic starch granules and tissues of each have been found under the microscope that we gain a definite idea of the nature of the constituents.

Again, in the examination of paper, the microscope is our sole dependence in learning the nature and approximate percentages of the fibers employed, chemical analysis serving merely to determine the kind and amount of sizing, coating and other non-fibrous constituents.

Among some condimental cattle foods examined by the writer some time since was one, the chemical analysis of which disclosed but one proximate constituent, viz., common salt; the microscope, however, disclosed linseed meal, corn meal, wheat feed, mustard hulls, cocoa shells, malt sprouts, fenugreek and turmeric. In such a case, dependence must be placed entirely on the microscope, except for mineral ingredients.

Chemical analysis of another sample demonstrated the presence of ground bone, carbonate of lime, iron oxide and free sulphur; microscopical examination disclosed linseed meal, wheat feed and charcoal. This is a striking example of a material in which half the constituents (all mineral) can only be detected by chemical analysis; the other half (all vegetable) by the microscope.

Many other equally striking examples of the interdependence of these two applied analytical sciences might be cited.

The point now arises as to who is to carry on these two lines of investigation so different in details, but so similar in purpose.

One plan is for a chemist to make the chemical analysis and a botanist the microscopical examination. This plan has the advantage that each can confine his attention to one specialty, but it had the disadvantage that the close partnership between the two, which is essential to the best results, outside of large institutions, is both difficult and expensive. Such a division of labor would usually be as impracticable as to divide the work of a chemical laboratory between a chemist and a physicist, the former conducting the precipitations and other chemical processes, the latter, polarizations, determinations of specific gravity, refractive index and the like.

The rational plan is for one man to master both lines of research. Such a man need not execute all the details, but he should be thoroughly acquainted with them and should interpret the results. We will call him an analyst, not a chemist or a botanist, and his laboratory an analytical laboratory, not a chemical or botanical laboratory. His equipment should consist of the necessary apparatus for a wide variety of chemical work and a complete microscopical outfit, including micro-reagents and a set of standard

specimens of economic seed, roots, barks, fibers, woods, etc.

But in order to have workers in this field, we must have suitable courses of instruction in our schools of science. The subject has a recognized place in many continental universities, particularly in the schools of medicine, pharmacy and hygiene, but outside of a few institutions, receives little attention in America.

The student who seeks to prepare himself for this field should take both chemical and botanical studies. In chemistry, he should study the branches taught in a well-regulated chemical course—elementary chemistry, qualitative and quantitative analysis, organic and physical chemistry, and so on. In botany he should take up successively elementary botany, systematic botany (at least of the phanerogams) and vegetable anatomy and physiology. These studies are all on the curriculum of every college and school of technology, although the student of chemistry does not usually take all the botanical studies named. Without a certain amount of botanical training, however, a chemist is no more fitted to take up microscopical analysis than a botanist without chemical training is fitted to work at quantitative analysis.

After his preliminary studies in chemistry and botany, the student is ready to take up a course in the methods for the chemical and microscopical examination of the various raw materials and of the products derived from them. This course should be so arranged that the student will carry along his chemical and histological practice side by side, as he must do afterwards in practical work. For example, in studying the cereal grains, he should devote part of his time to the methods of determining water, ash (including ash analysis), protein, fiber, starch, fat, pantosans, etc., and another part to a systematic study of the starches and the histological elements of the bran coats, both in sections and in powdered form. In like manner, he should take up a chemical and histological study of leguminous seeds, oil seeds, spices, tea, coffee, cocoa, drugs, fibers, etc.

His work in the chemical laboratory should teach him not only the strictly chemical methods, but also the use of the polariscope, the spectroscope and other physical apparatus, and his microscopical instruction should fit him not only to differentiate organized forms, but other characteristic elements, such as fat crystals, mineral crystals, and the like.

After such a course, he should be able not only to undertake investigations in physiological or plant chemistry, but also the laboratory work of an official food department or a custom house, a flour mill, a brewery, a sugar refinery, a candy works, a fruit cannery, a drug mill, a textile mill, a paper mill, etc.

It is my firm belief that courses similar to that outlined should be conducted in all our leading universities and schools of technology, and the student should be taught the use of the microscope in conjunction with the balance in solving the analytical problems which every day become more numerous and intricate.

COST OF GAS MANUFACTURE.

Mr. J. T. Newbigging, the engineer of the Manchester (England) city works, in February gave at the Manchester University the first of two lectures on gas manufacture, gas works construction and gas works management. The following abstract of the lecture is taken from the Daily Consular and Trade Reports.

Mr. Newbigging said that about $630,000,000 to $680,000,000 was invested in coal-gas manufacture and distribution in the United Kingdom alone, in addition to enormous sums in manufactories engaged in the manufacture of gas appliances for its utilization. The statement that no important improvements had been made in gas manufacture since the early days of its introduction is altogether wide of the truth. As a matter of fact, great improvements had been made in plant and apparatus, while the mechanical and chemical principles involved in gas production are now carefully investigated by gas engineers and are yearly becoming better known. He detailed the considerations which are involved in choosing a site for a gas works, and put the area required at from 1½ to 2 acres per million cubic feet a day. He gave also some interesting figures for the cost of works and distributing plant. The capital of large undertakings, he said, might be taken at about £500 ($2,433) a million cubic feet a year, of which half would be for the cost of land, buildings and manufacturing plant; $1,158 for the cost of distributing plant, and the rest for the cost of tar-distilling plant, and so on. Mains would cost $516 out of the $1,158 for distributing plant; service pipes, $170; ordinary meters, $170; automatic meters, $122; gas cookers and fires, $180. These costs assume that 65 per cent of the consumers are using gas through ordinary meters, 35 per cent through automatic meters, and that one-third of the customers use gas for heating and cooking.

The average cost of producing and distributing lighting gas in England was, Mr. Newbigging said, roughly two-thirds of the selling price. The net cost of coal where the selling price was 2s. (48⅜ cts.) a thousand feet would be made up by the working expenses; and the other 8d. (16 cts.) would be absorbed in the case of a municipal undertaking in the discharge of the interest on the borrowed capital and the provision of a sinking fund, and, unfortunately in many cases, the payment of a large sum in relief of taxes.

In the course of some later remarks on the carbonization of coal, he compared the horizontal and vertical retort systems, and gave his reasons for preferring the latter, the continuous carbonization system. Although the cost of construction was 15 per cent to 20 per cent above the cost of a horizontal retort, yet the cost of carbonizing was only half, and double the quantity of gas could be produced on the same area of land. The fuel cost was as low as 9 per cent (i. e., 9 lbs. of coke to 100 lbs. of coal carbonized). The Manchester gas committee, after using the vertical system at Droylsden, had decided, he said, to put it in at another of its works.

CONVERTING PEAT MOORS INTO GAS AND ELECTRICITY.*

During many years the Prussian Government has endeavored to secure the utilization of the extensive moore in the neighborhood of Bremen, in the Province of Hanover, and large sums of money and great efforts have been expended for this purpose. A "Moor experiment station" was located at Bremen, where means and ways were studied, and experiments with the soil of the moors were made to discover a method whereby these extensive waste lands might be brought under cultivation, and induced to yield their proper share of production.

Peat, being a poor man's coal, does not permit heavy shipping charges, and as the consumption of peat produced even in the more easily accessible districts had rather decreased, coal and gas having taken its place in many households, a way had to be found to utilize the peat at its place of production, or in the moor itself.

After several trials this was accomplished by making use of the great sources of power contained in the vast masses of peat, and at the same time improving the soil and making it fit for farming.

POWER PLANT—ELECTRICITY.

The Government, out of its desire to have the lands cultivated, had dug, at its own expense, drainage canals in the governmental districts of Aurich, East Frisia. The transportation of the great quantities of peat, dug out on this occasion, to the larger peat-consuming cities was too expensive, and it had to be disposed of in some other manner. Thereupon the Government erected a power station in a convenient location on the land to be drained, using the peat as fuel. Thus originated the power plant at the Friedeburger Wiesmoor.

Shortly after establishment this plant was sold to the Siemens Elektrische Betriebe, which enlarged it considerably. It now supplies electricity to the cities of Norden, Emden, Aurich, Bant, Wilhelmshaven, and also to a large rural district.

In establishing the gas and electricity plant in the Schweger Moor, Province of Hanover, ideas and methods were carried out similar to those which proved of practical worth in the founding and development of the Friedeburger Wiesmoor plant.

For the purpose, however of obtaining certain valuable by-products there was followed at the Schwegermoor plant the advice of the experts, Geheimrat Prof. Dr. A. Frank, Charlottenburg, and Dr. N. Caro, Berlin. The peat is gasified, leaving sulphate of ammonium, a valuable fertilizer, and tar as by-products in sufficient quantities to meet the running expenses of the plant. The gas is used as fuel in generating electricity, while the tar serves as fuel under the gas generators.

This indirect way of making use of peat as fuel has one great advantage which must not be underestimated. It is generally known that in order to advantageously use peat as fuel the peat must not contain more than 30 per cent humidity. In this climate of nearly constant dampness it is very difficult to obtain dry peat in such quantities as would be needed for fuel by such a large plant. As peat, for gasification, may contain up to 70 per cent humidity, it is much easier to supply the plant with the necessary quantity, the more so as under such circumstances peat gathering may be extended until late in the fall.

To run the new plant Hannoversche Kolonisations und Moorverwertungs Gesellschaft, a limited stock company, was formed, with headquarters at Osnabrueck. This company purchased the Schweger Moor which covers about 2,471 acres, and is in the Kreise (district of) Wittlage and Bersenbrueck, near the city of Osnabrueck. In the spring of 1910 construction of the plant was begun, and on October 2, 1911, the first electricity was supplied.

METHODS OF OPERATION.

The peat which is to be gasified is broken up by a tearing machine and then passes from the bunker into the generator. The gas obtained undergoes a purifying process and is said to be ultimately absolutely pure. The salt obtained by this method is said to be also of good quality. The following will illustrate a good average result of the working process at this plant:

During December, 1911, there were gasified 1,325 metric tons (1,000 kilos = 1 metric ton = 2,204.6 pounds) of raw peat, of 60 per cent humidity, being equal to 530 tons of absolutely dry peat. The fuel used in this particular process consisted of 170 tons of raw peat, of the same humidity, equal to 68 tons of dry peat, together with some tar. It may be observed that the use of peat as a fuel has since been discontinued, tar alone being now used in operating the plant.

The above mentioned 530 tons of dry peat produced as a by-product 18.3 tons of salt, or 34.5 kilos, per metric ton of dry peat, containing about 1 per cent of nitrogen. This means that about 75 per cent of the nitrogen contained in the peat has been made useful in the form of sulphate of ammonium—a very favorable result.

The above-mentioned 530 and 68 tons, equalling 598 tons of dry peat, produced 427,000 kilowatt (hours) power, or 715 kilowatt hours, per metric ton of dry peat, being about the same as 1,000 electric horsepower (for one hour) to the ton of dry peat.

*From the Daily Consular and Trade Reports.

Among the many branches of the Russian metal industry, the manufacture of copper is remarkable for its rapid development. Seven years ago the 10,000 tons that constituted the output of all the existing works did not meet even half of the requirements of the country. In 1907 the Russian production was 14,750 tons; in 1910, 23,000 tons; 1911, 26,500 tons; and during six months of 1912 the total output was 16,600 tons.

Briquet Production in the United States in 1912.

The quantity of briquetted fuel manufactured in the United States in 1912 showed a small gain over the output for 1911, and according to E. W. Parker, of the United States Geological Survey, the briquet industry may be considered as now passing out of the experimental stage and assuming a more substantial and permanent character. The quantity of briquetted fuel made in 1912, at 19 plants, was 220,064 short tons, valued at $952,261, as compared with 218,443 tons valued at $808,721 in 1911. Of these plants, 7 used anthracite culm, 9 used bituminous or semi-bituminous slack, 1 used residue from gas manufactured from oil, 1 used mixed anthracite culm and bituminous slack, and 1 used peat. The largest producer of briquets in the United States in 1912 was the Berwind Fuel Company, of Superior, Wis., the output of which was a little in excess of 50,000 short tons. The plant has a capacity of between 35 and 40 tons of briquets an hour.

The quantity of raw material available for the manufacture of briquets, as stated by Mr. Parker, is ample, and may be obtained at slight cost. The most desirable material for producing a smokeless product is anthracite culm, a plentiful supply of which still remains in the anthracite region of Pennsylvania, and more is produced daily in the mining operations. It is not too much to believe or to hope that in the near future the small sizes of anthracite, such as buckwheat and smaller, that are now sold for making steam, in competition with bituminous coal and at prices below the actual cost of production, will become more valuable as a raw material for the briquet manufacturer. The output of these small sizes, produced by breaking up large coal to obtain the domestic grades—egg, stove and nut—exceeds 20,000,000 long tons annually, exclusive of 3,000,000 to 4,000,000 tons annually recovered from the culm banks by washeries. The present revenue from this product will not exceed $30,000,000. Washery and small size coal is worth from 50 cents to $1.50 a ton, the price depending on the size. As briquetted fuel it should be worth as much as stove or egg coal, or $3 to $4 per ton. The cost of briquetting is $1 to $1.25 per ton. The uniform size of the briquets makes them highly desirable as a domestic fuel; besides, if properly made, they are completely consumed, and do not produce that bugbear to the housekeeper, clinkers.

One objection raised to the use of briquets is that they will compete with the prepared sizes of anthracite. From the viewpoint of the consumer, the objection lacks logic, and this seems more evident when the apparent profit obtainable on the briquetted product is considered.

Slack from noncoking, bituminous, subbituminous and semianthracite coals is another cheap and abundant raw material. It is obtainable in all the coal mining regions of the middle west, where at many places it is now wasted or almost given away. Some slack piles have been burned to prevent their cumbering the ground; others have ignited spontaneously and devoured themselves. The 220,064 tons of briquets made in 1912 represent but a drop taken from the bucket of available material.

The vast and almost untouched areas of lignite in North Dakota and Texas still contain enormous supplies of fuel that European experience has taught is well adapted to briquetting and that is much more usable in that form than in the raw state. The School of Mines of the North Dakota University has been making some interesting and valuable experiments in briquetting lignite, under the direction of Prof. E. J. Babcock, and has already attained excellent results.

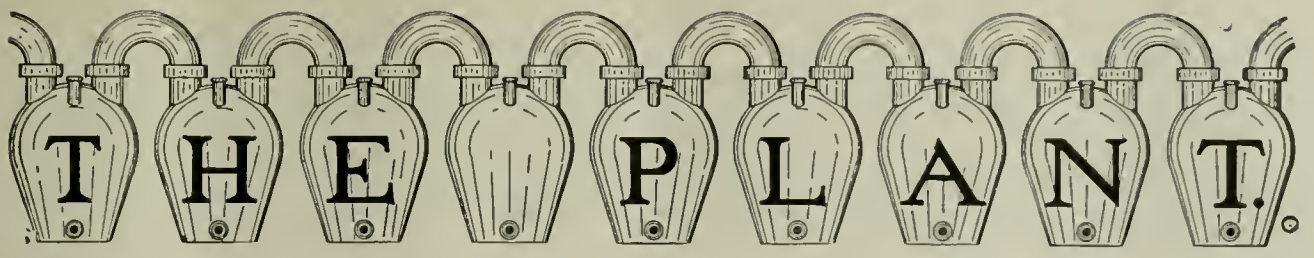
The large areas of peat beds in the United States are also available as a source of raw material. They are generally remote from the coal fields, and briquetted fuel from peat, when properly prepared, makes an excellent substitute for coal. The peat now produced in the United States is used for stable litter, fertilizer, etc. None is used for fuel.

While the briquet industry in the United States is still in its infancy, the following figures show that the production has nearly twice doubled since 1907:

Year.	Short tons.	Value.
1907	66,524	$258,426
1909	139,661	452,697
1911	218,443	808,721
1912	220,064	952,261

A Reuter dispatch from Singapore states that a demonstration of the process of curing raw rubber with vapor was carried out on the Sione estate at Kuala Lumpur in the presence of the Chief Secretary, the Director of Agriculture, and a number of planters. The process occupied two hours.

The President has recently approved the withdrawal of three tracts of land of the desert-basin type in California and Nevada that are believed, as the result of investigations by the United States Geological Survey, to contain valuable deposits of potassium salts and brines. The Survey adds: The constructive good faith of the Government in the withdrawal of these lands in aid of legislation is indicated by the fact that concurrently with the withdrawal the Interior Department has prepared the draft of a law intended to relieve the present chaotic situation and provide a safe and sure legal basis for the development of the deposits now known and that may be discovered in the future. This draft has been submitted to Congress for its consideration, and its enactment will be urged in order that American potash deposits may be developed under conditions that are favorable to the producer and will at the same time protect the consumer.



THE ELECTRODEPOSITION OF BRASS AND BRONZE.*

By C. W. BENNETT.

The solutions used for the deposition of these alloys are those in which the concentration of copper as ion is low. They are, therefore, solutions of complex salts. The difficulty experienced in the deposition of brass is not so great as that encountered with bronze. In the former case it is only necessary to obtain a solution in which the voltages required to deposit the two metals are as close together as possible. Having obtained this, the current density and relative concentration of the metals in the solution may be varied until the deposit contains both metals in the desired proportions. In the case of bronze, however, another condition is introduced which is practically very hard to regulate. Substitution of tin for zinc introduces the possibility of the oxidation of tin and also of its dissolving and forming a colloid. In this case there is a possibility of depositing metals existing in the solution in the following forms: Cupric, cuprous, stannous and stannic ions and as colloidal oxide. Some of the bronzing solutions give lovely deposits for a short time. After running for a while the deposit becomes rich in either copper or tin. This is due to the fact that some of the changes mentioned above have altered the solution so that the original conditions no longer obtain. The most important changes, it is believed, are the oxidation of the tin over to the stannic condition, and the formation of the colloidal oxide. A plating can be obtained therefore, if a large volume of the solution be used or if a new solution be continuously run in. No solution, however, gives satisfactory plate continuously. As may be expected, therefore, while brass is plated commercially, no satisfactory solution has ever been suggested for bronze. The solutions recommended for these depositions are given below.

PART I. BRASS.

Heeren's[1] solution is the following:

Copper sulphate	3 grams
Zinc sulphate	26 grams
Potassium cyanide	66 grams
Water	1 liter

Roseleur recommends three solutions.[2] The first is:

Copper carbonate, freshly precipitated	12.0 grams
Zinc carbonate, freshly precipitated	7.0 grams
Potassium cyanide	20.0 grams
Sodium carbonate	20.0 grams
Sodium bisulphite	20.0 grams
Arsenious acid	0.2 grams
Water	1.0 liter

For all metals this bath is recommended:

Copper acetate	12.5 grams
Zinc chloride	12.5 grams
Sodium carbonate	30.0 grams
Sodium bisulphite	20.0 grams
Potassium cyanide	35.0 grams
Arsenious acid	0.2 grams
Water	1.0 liter

It is stated that these solutions should be boiled before being used. Working for several hours is said to make them work better. The amount of sodium carbonate may be increased to about 90 grams per liter if iron is to be plated.

Lastly, the following is recommended for coating zinc:

Copper acetate	14 grams
Zinc chloride	14 grams
Sodium bisulphite	28 grams
Potassium cyanide	30 grams
Ammonia (sp. gr. 0.9)	16 grams
Water	1 liter

Cuproso-cuprie sulphite or cuprous oxide may be used in the preparation of the brassing solution. A solution from cuprous oxide will be given.[3]

Cuprous oxide	8.5 grams
Zinc chloride	8.0 grams
Potassium cyanide	30.0 grams
Sodium bisulphite	20.0 grams
Water	1.0 liter

Copper and zinc cyanides or potassium cupro- and potassium zinc cyanides may also be used, the final solution being practically the same as those given above.

Gore[4] recommends this solution for iron:

Copper acetate	12.5 grams
Zinc chloride	10.0 grams
Potassium cyanide	38.0 grams
Sodium carbonate	100.0 grams
Sodium bisulphite	20.0 grams
Water	1.0 liter

Morris and Johnson[5] recommend the following:

Copper cyanide	12.5 grams
Zinc cyanide	6.2 grams
Potassium cyanide	100.0 grams
Ammonium carbonate	100.0 grams
Water	1.0 liter

The concentration of cyanide is so high here that it is doubtful whether deposition will occur, except at a high temperature or with a high current density.

*Paper to be presented at the 23rd General Meeting of the American Electrochemical Society, at Atlantic City, N. J., April 3-5, 1913.

[1]The references given simply to name and page refer to the books of these authors. Watt and Philip: p. 381; McMillan: p. 283.

[2]Langbein: p. 324; Brannt: p. 239; McMillan: p. 283; Watt and Philip: p. 381.

[3]Langbein: p. 326.

[4]Langbein: p. 328; Brannt: p. 242.

[5]Brannt: p. 242; McMillan: p. 283; Watt and Philip: p. 380.

[6]Brannt: l. c., p. 243.

Pfanhauser[6] recommends the following for coating upon all metals:

Copper cyanide	42 grams
Zinc cyanide	42 grams
Potassium cyanide	4 grams
Ammonium chloride	4 grams
Ammonia-soda	20 grams
Water	1 liter

Another solution[7] is the following:

Copper chloride	5.0 grams
Zinc sulphate	10.0 grams
Potassium cyanide	2.4 grams
Potassium carbonate	120.0 grams
Ammonium nitrate	61.0 grams
Water	1.0 liter

Several other solutions differing slightly from the above[8] may be given:

Copper chloride	7.5 grams
Zinc sulphate	15.0 grams
Potassium carbonate	180.0 grams
Ammonium nitrate	90.0 grams
Water	1.0 liter

Another solution is:

Copper chloride	5.5 grams
Zinc sulphate	8.0 grams
Potassium carbonate	65.0 grams
Potassium cyanide	10.6 grams
Water	1.0 liter

Russell and Woolrich's solution contains the following:

Copper acetate	150 grams
Zinc acetate	15 grams
Potassium acetate	150 grams
Potassium cyanide	to dissolve precipitate first formed
Water	1 liter

Walenn recommends the following:

Copper nitrate	Saturated solution
Zinc sulphate	Saturated solution
Ammonium hydroxide	Sufficient to redissolve hydroxides
Potassium cyanide	In excess

Salzede's solution is the following:

Copper chloride	3 grams
Zinc sulphate	7 grams
Potassium cyanide	10 grams
Potassium carbonate	100 grams
Water	1 liter

Watt's solution is:

Copper acetate	4.5 grams
Zinc sulphate	9.0 grams
Potassium cyanide	7.5 grams
Potassium hydroxide	67.0 grams
Ammonium hydroxide	30.0 grams
Water	1.0 liter

A patented[9] solution contains:

Copper carbonate (freshly precipitate)	35 grams
Zinc oxide	23 grams
Potassium cyanide	165 grams
Potassium carbonate	75 grams
Water	1 liter

The addition of cupric ammonide ($Cu_2O.4NH_3$)[10] is said to aid the deposition of a good brass plate.

Some commercial brass plating solutions may be given:

Copper carbonate (dry)	50 grams
Zinc sulphate	30 grams
Potassium cyanide	75 grams
Water	1 liter

Copper anodes are used and zinc salt added from time to time.

[7]Fontaine: p. 145; McMillan: p. 283; Watt and Philip: p. 378.
[8]Fontaine: p. 146; McMillan: p. 283; Watt and Philip: p. —.
[9]U. S. Pat., 34,640.
[10]Phil. Mag. [4], 1, 43 (1871).
[11]National Electroplaters' Assoc., March 29, 1912.

Another solution used is the following:

Copper carbonate	50.0 grams
Zinc carbonate	10.0 grams
Potassium cyanide	110.0 grams
Sodium carbonate	14.0 grams
Sodium bisulphite	3.5 grams
Ammonium hydroxide	7.0 grams
Water	1.0 liter

Another combination[11] highly recommended is the following:

Solution 1:

Copper sulphate	112 grams
Potassium cyanide	112 grams
Sal soda	69 grams
Potassium hydroxide	5 grams
Water	⅔ liter

Solution 2:

Zinc sulphate	37 grams
Potassium cyanide	35 grams
Sal soda	25 grams
Potassium carbonate	6 grams
Water	⅓ liter

The current is started on solution 1, and, while working slowly, solution 2 is added slowly until the desired brass is obtained.

These solutions are all made up to give a brass containing 30 to 40 per cent zinc. Consequently anodes of this composition are used.

A solution used in the laboratory at Cornell contains:

Copper sulphate	25 grams
Zinc sulphate	29 grams
Potassium cyanide	to dissolve the precipitate
Water	1 liter

These solutions are tabulated in Table I.

PART II. BRONZE.

Bronzing solutions are also numerous. The most striking fact, however, is that practically all of them are impracticable. None that has been tried personally gives a satisfactory plate. Commercially, of course, the bronze color is imitated with brass, or by coloring with some reagent.

A patented solution[12] contains:

Copper carbonate	37.5 grams
Tin oxide	7.5 grams
Potassium carbonate	15.0 grams
Potassium cyanide	202.5 grams
Water	1.0 liter

Failing to obtain good deposits with any of the solutions recommended by plating handbooks, Langbein recommends[13] the following:

Solution 1:

Sodium pyrophosphate	50 grams
Water	1 liter

To this solution are added the following 2 solutions 2 and 3 in proportions depending on the composition bronze desired:

Solution 2:

Sodium pyrophosphate	Saturated solution
Copper phosphate	To saturation

Solution 3:

Sodium pyrophosphate	Saturated solution
Stannous chloride	To saturation

If the deposit is too light more copper solution is added; if too dark, more tin. The anodes of cast bronze are said to dissolve readily in the solution.

[12]U. S. Pat., 34,640.
[13]Langbein: p. 337; Brannt: p. 248.

Salzède's[14] solution, to be used at 30° to 35° C., is:

Cuprous chloride	1.5 grams
Stannous chloride	1.2 grams
Potassium cyanide	10.0 grams
Potassium carbonate	100.0 grams
Water	1.0 liter

Elsner's solution[17] is the following:

Copper sulphate	7.0 grams
Stannic chloride	8 grams
Potassium hydroxide	Small amount
Water	1 liter

TABLE I.—SOLUTIONS FOR THE DEPOSITION OF BRASS.
Parts by weight of igredients to 1,000 parts of water.

	Copper Sulphate.	Copper Carbonate.	Copper Acetate.	Copper Cyanide.	Cuprous Oxide.	Copper Chloride.	Copper Nitrate.	Zinc Sulphate.	Zinc Carbonate.	Zinc Chloride.	Zinc Cyanide.	Zinc Acetate.	Zinc Oxide.	Potassium Cyanide.	Sodium Carbonate.	Sodium Bisulphide.	Arsenious Acid.	Ammonium Hydroxide.	Ammonium Carbonate.	Ammonium Chloride.	Ammonia-Soda.	Ammonium Nitrate.	Potassium Carbonate.	Potassium Acetate.	Potassium Hydroxide.	Sal Soda.	Water.
1	3	..	..	..	..	..	..	26	..	..	..	..	..	60	..	..	..	..	..	..	..	..	..	..	..	..	1,000
2	..	12	..	..	..	..	..	..	..	..	..	..	..	20	20	20	0.12	..	..	..	..	..	..	..	..	..	1,000
3	..	..	13	..	..	..	..	..	..	13	..	..	..	35	30	20	0.12	..	..	..	..	..	..	..	..	..	1,000
4	..	..	14	..	..	..	..	..	..	14	..	..	..	30	..	28	..	16	..	..	..	..	..	..	..	..	1,000
5	..	..	..	..	9	..	..	..	..	8	..	..	..	30	..	20	..	..	..	..	..	..	..	..	..	..	1,000
6	..	..	13	..	..	..	..	..	..	10	..	..	..	38	100	20	..	..	..	..	..	..	..	..	..	..	1,000
7	..	..	..	13	..	..	..	..	..	..	..	..	..	100	..	..	..	..	100	..	..	..	..	..	..	..	1,000
8	..	..	..	42	..	..	..	..	..	..	42	..	..	4	..	..	..	..	..	4	20	..	..	..	..	..	1,000
9	..	..	..	..	..	5	..	10	..	..	..	..	..	24	..	..	..	..	..	..	..	61	120	..	..	..	1,000
10	..	..	..	..	..	8	..	15	..	..	..	..	..	..	..	..	..	..	..	..	..	90	180	..	..	..	1,000
11	..	..	..	..	..	6	..	8	..	..	..	..	..	10	..	..	..	..	..	..	..	..	65	..	..	..	1,000
12	..	..	150	..	..	..	..	..	..	..	..	15	..	q. s.	..	..	..	..	..	..	..	..	..	150	..	..	1,000
13	..	..	..	..	..	..	s.	s.	..	..	..	..	..	ex	..	..	..	q.s.	..	..	..	..	..	..	..	..	1,000
14	..	..	..	..	..	3	..	7	..	..	..	..	..	10	..	..	..	..	..	..	..	..	100	..	..	..	1,000
15	..	..	4.5	..	..	..	..	9	..	..	..	..	..	7.5	..	..	..	30	..	..	..	..	..	..	67	..	1,000
16	..	35	..	..	..	..	..	..	..	..	..	..	23	165	..	..	..	..	..	..	..	..	75	..	..	..	1,000
17	..	50	..	..	..	..	..	30	..	..	..	..	..	75	..	..	..	..	..	..	..	..	..	..	..	..	1,000
18	..	50	..	..	..	..	..	..	10	..	..	..	..	110	14	4	..	..	..	..	..	..	..	..	..	..	1,000
19	112	..	..	..	..	..	..	37	..	..	..	..	..	147	..	..	..	..	..	..	..	..	6	..	5	94	1,000
20	25	..	..	..	..	..	..	29	..	..	..	..	..	q. s.	..	..	..	..	..	..	..	..	..	..	..	..	1,000

Gountier's solution for plating wrought and cast iron is the following:[15]

Potassium ferrocyanide	30 grams
Cuprous chloride	15 grams
Stannous chloride	40 grams
Sodium thiosulphate	40 grams
Water	1 liter

Solutions recommended by Weiss[18] are the following:

Cupric chloride	20 grams
Stannous chloride	10 grams
Potassium carbonate	100 grams
Potassium cyanide	10 grams
Water	1 liter

TABLE II.—SOLUTIONS FOR DEPOSITION OF BRONZE.

	Copper Carbonate.	Copper Phosphate.	Cupric Chloride.	Cuprous Chloride.	Copper Cyanide.	Copper Sulphate.	Tin Oxide.	Stannous Chloride.	Stannic Chloride.	Stannous Oxalate.	Sodium Stannate.	Potassium Carbonate.	Potassium Cyanide.	Sodium Pyrophosphate.	Potassium Ferrocyanide.	Sodium Thiosulphate.	Potassium Hydroxide.	Rochelle Salt.	Soda Lime.	Ammonium Oxalate.	Oxalic Acid.	Water.
1	37.5	..	..	..	..	..	7.5	..	..	..	..	15	203	..	..	..	..	..	..	..	..	1,000
2	..	q.s.	..	..	..	..	..	q.s.	..	..	..	..	..	50	..	..	..	..	..	..	..	1,000
3	..	..	..	1.5	..	..	..	1.2	..	..	..	100	10	..	..	..	..	..	..	..	..	1,000
4	..	..	..	15	..	..	..	40	..	..	..	..	..	..	30	40	..	..	..	..	..	1,000
5	..	..	..	..	5	..	2	..	..	..	..	..	40	..	..	..	..	..	..	..	..	1,000
6	..	..	..	..	..	70	..	..	8	..	..	..	..	..	..	..	q.s.	..	..	..	..	1,000
7	..	..	20	..	..	..	..	16	..	..	..	100	10	..	..	..	..	..	..	..	..	1,000
8	..	..	..	..	..	64	..	..	9	..	..	..	128	..	..	..	q.s.	..	..	..	..	1,000
9	..	..	..	..	..	35	..	..	..	..	q.s.	..	..	..	..	..	..	150	80	..	..	1,000
10	..	..	..	..	..	15	..	..	..	4.2	..	..	..	..	..	..	..	..	..	55	5	1,000
11	..	..	..	..	..	22	..	..	..	..	5.5	..	..	..	..	..	5	150	..	..	..	1,000

Roulz's solution[16] contains:

Copper cyanide	5 grams
Tin oxide	2 grams
Potassium cyanide	40 grams
Water	1 liter

This gives a more concentrated solution of copper and tin than Salzède's solution. The other solution recommended by Weiss contains:

Copper sulphate	61 grams
Stannic chloride	9 grams

[14]Langbein: p. 336; Brannt: p. 247; McMillan: p. 287; Fontaine: p. 146.
[15]Brannt: p. 247.
[16]Brannt: p. 247; McMillan: p. 247.
[17]Brannt: p. 247; McMillan: p. 287.
[18]McMillan: p. 287.

Potassium cyanide	128 grams
Potassium hydroxide	Small amount
Water	1 liter

Weil's solution[19] follows:

Copper sulphate	35 grams
Sodium stannate	Sufficient to give required bronze
Soda-lime	80 grams
Rochelle salt	150 grams
Water	1 liter

A solution recommended by Currie[20] contains:

Copper sulphate	15.0 grams
Stannous oxalate	4.2 grams
Ammonium oxalate	55.0 grams
Oxalic acid	5.0 grams
Water	1.0 liter

Another solution[21] which does not give satisfaction is the following:

Copper sulphate	22.0 grams
Sodium stannate	5.5 grams
Sodium hydroxide	5.0 grams
Rochelle salt	150.0 grams
Water	1.0 liter

These solutions are tabulated in Table II.

NOTES ON THE CHEMISTRY OF PAPERMAKING.*

By THOMAS J. KEENAN, F. C. S.

In an address before the King's County Pharmaceutical Society in the Brooklyn College of Pharmacy on January 14, 1913, the managing editor of Paper described some of the operations involved in the manufacture of woodpulp and paper, contrasting them with the work of the pharmaceutical chemist. He demonstrated among other things that the same uncertainty which formerly prevailed in pharmaceutical work—and which still exists to some extent—regarding the extractive or alkaloidal strength of the ultimate tincture or extract is experienced by the papermaker in regard to the nature of the product he may obtain after extracting his wood and mixing the residuum with varying proportions of other materials, such as clay, alum and rosin, in a beater—the modern analogue of the stamping machine or crude mortar and pestle of the mediæval craftsman.

The application of chemistry to papermaking began with the process of treating wood with caustic alkalis or alkaline earths so as to extract a product to replace the pulp made from rags. It had not been overlooked, of course, that the use of chlorine bleach came first, following the discovery of chlorine by Scheele in 1774.

The timber, from which the pulp or cellulose destined to form the finished sheet of paper is produced, varies in quality according to cultivation, soil and climatic influences in much the same way as do the drug-producing plants, and the quality and quantity of pulp varies according to the class of woods used and the nature of the process, so that uniformity of product is nearly as difficult in the one case as in the other.

The production of a finished paper of uniform and unvarying quality and characteristics, as determined by chemical and microscopical tests, is impracticable, owing to conditions inherent in the process of manufacture. The papermaker cannot tell to a nicety what proportion of the materials which go to make up his "furnish" or formula will be retained in the ultimate paper and what will go out with the water which is drained away from the pulp as it travels on the running wire of the paper machine to the press and drying rolls. In this respect the art of papermaking has not kept pace with the progress of other arts and crafts, though in the direction of mechanical improvements there are few industries in which mechanical invention has been so highly developed or in which engineering as a science plays a more important part, some of the special machinery in the equipment of a modern paper mill being examples of engineering skill that are little short of marvelous in the ingenuity of their construction and operation.

In the primary processes of separating the pulp or cellulose from the wood the pharmacist will see no analogy with any operation known to his art. On the contrary, he will observe methods employed and results obtained as astounding by their destructive wastefulness as by total opposition to galenical methods in the extraction of valuable plant constituents. It is in the intermediate and later stages of papermaking—in the combining of the "furnish", as the assembled ingredients of the formula for a given paper are conveniently termed, and in the testing of papers—that he will note familiar combinations and reactions.

The simplest form of woodpulp, that known as "ground wood," which forms the body of newsprint paper, is produced by pressing logs of cone-bearing trees, such as spruce, balsam, pine and fir, freed from bark, and cut into short pieces about two feet long, against revolving grindstones, under a stream of water, so that the disintegrated pulpy fibers, torn away from the log, obliquely or against the grain, can be run off into tanks and thence flowed away to undergo a screening and straining operation for the removal of refuse and unground lumps. As the pulp obtained in this way contains the sap, lignin and resin of the raw wood, substances that are prone to rapid oxidation and discoloration, paper made from it soon deteriorates, becoming brown and brittle, and it is a very perishable product. Pulp of this kind, however, is only used as an admixture with chemically prepared pulp in the manufacture of newsprint and the cheaper grades of book paper, or alone in the manufacture of boards; ground poplar wood being also used to some extent for this purpose.

It is the pulp produced by chemical means which has most interest for the pharmacist, the systems in use being, as already indicated, so much at variance with pharmaceutical work and especially the extractive processes employed in pharmacy. The chief processes are known as the sulphite, the soda and the sulphate. By the solvent action of the chemical solutions

[19]McMillan: p. 287.
[20]Jour. Phys. Chem., 10, 515 (1906).
[21]Bennett: p. 266.
*From Paper.

upon the nonfibrous constituents of the wood the cellulose is set free from its enveloping bodies and is recovered to the extent of nearly 50 per cent of the total weight of the wood. The material which is extracted, consisting of all the soluble constituents of the wood —the gums, resins, tannins and the other valuable plant principles which encrust the cellulose—represents to the papermaker so much offal or waste, and, in the soda process, is destroyed by burning the soda being recovered; and, in the sulphite process, washed into rivers and streams, with a total loss of organic extractives and chemicals.

It is scarcely necessary to emphasize more particularly the sharpness of the contrast that is here presented to the work of the pharmacist, where the end aimed at is the separation of the active and soluble constituents of the plant from the inert insoluble portion; the residue or marc, consisting of broken down woody tissue and fibers, being rejected. But to illustrate better the contrast in work, a brief description of the sulphite process of pulpmaking may be given. The wood, having been cleaned and cut up into pieces from two to five feet in length, as in the ground wood process, is chipped up into small pieces or chips about one-fourth inch to one-half inch thick and boiled under pressure in large steel digesters capable of holding twenty tons of wood at one operation and yielding ten tons of finished pulp. The digesters are lined with heavy cement backing faced with brick, pointed with litharge and glycerin, to prevent contact with the metal.

The sulphite liquor in which the wood is boiled is made by passing sulphur dioxide—obtained by burning sulphur, or iron pyrite, in special ovens—into tanks filled with water and a known quantity of slaked lime tion of a solution of the acid sulphites of calcium and magnesium, which is the active solvent agent. The (prepared from dolomite). This results in the formachemistry of the reaction between the wood and the sulphite liquor prepared from dolomite or magnesian limestone is tersely but sufficiently stated by Thorp ("Outlines of Industrial Chemistry." Macmillan, 1911), who explains that the acid sulphites react much like sulphurous acid, but the sulphites combine with the aldehydes formed in the first stages of the decomposition, producing stable and soluble double salts. The organic acids which are also formed decompose the bisulphites and form soluble calcium and magnesium salts, while the sulphurous acid gas is set free, causing a constant increase of pressure within the digester. The acid sulphites also tend to bleach the coloring matter of the fibers by forming colorless compounds with them, but this is a very unstable bleach and the original color soon returns when the pulp is made into paper. Bisulphite of calcium is unstable and decomposes readily into neutral sulphite, setting free sulphurous acid. This results in the precipitation of the neutral sulphite on the fiber, which is left harsh even after long washing. Magnesium bisulphite is more stable, and although less corrosive to the fiber, it dissolves the noncellulose matter even more completely than does the lime salt; further any sulphate or neutral sulphite which may be formed is easily washed off and the pulp is left soft and white. Sodium bisulphite gives a better product than either of the foregoing, and strong liquors can be made from it; but it is too expensive for general use.

When the digesters have been filled with the wood chips and the requisite quantity of sulphite liquor is added, the manhole or cover at the top of the digester is securely fastened, and steam is turned on gradually until the pressure reaches seventy or eighty pounds. The cooking is steadily maintained at this pressure for a period of eight to ten hours. At the end of this time the contents of the boiler, consisting of softened pulp, are discharged into large vats and washed. The spent liquor containing the dissolved resinous and nonfibrous portions of the original wood is allowed to drain away from the mass in the tank, which is then washed out and made ready for another charge.

It is the disposition of this spent liquor which constitutes one of the weightiest problems confronting the manufacturer of chemical pulps today. He is eager to be informed of a means of utilizing the liquor that would obviate the present necessity of throwing it into contiguous rivers and streams, for he realizes the danger that threatens the industry from the enactment of laws that will prevent him from turning his waste liquors into the watercourses of the country in such large quantities as has been done up to the present time.

By neutralizing the liquor and starting fermentation of the contained sugars alcohol of a low grade is produced from it in several pulp plants in Sweden, and by a patented concentration process used in the United States, a compound is formed from the liquor, named glutrin, which is utilized as a binder in roadmaking, as a tanning extract and as an adhesive for sand in making molds and cores for iron castings in foundries.

But the profitable recovery of the organic matter dissolved from wood in the sulphite process is still an unsolved problem. The recovery of the innumerable organic substances dissolved in it, which is so fascinating a field of speculation for the chemist, has no interest for the pulpmaker, and is regarded as something of minor importance compared with the question of getting rid of the liquor in some way agreeable to the authorities and at the same time inexpensively and expeditiously. Although the problem has been deeply studied by able chemists for the past twenty years, it has yet to be tackled by a pharmaceutical chemist, and when it is we may look for the production of a whole series of new organic compounds.

In the soda and the sulphate processes of extraction there is effected a partial recovery of materials. By incinerating the spent soda liquor, after evaporating and concentrating it, the soda itself is regenerated, but there is here again a total loss of the organic deriva-

tives of the wood, which are burned up in recovering the soda.

The soda process is used for soft woods like poplar, cotton and basswood, whereas the sulphite process is exclusively employed for coniferous woods. The chipped wood is boiled in a solution of caustic soda for eight or nine hours at a pressure of seventy or eighty pounds. The pulp produced is soft and bleaches well, making it especially well adapted for the manufacture of book and magazine papers.

Sulphate pulp is prepared by boiling the wood chips in a solution of sodium sulphate containing some caustice soda and sodium carbonate. It is a slower process than either the sulphite or the soda, as the period of boiling instead of being eight or nine hours, is sometimes extended to thirty-five hours, though good results are possible with a shorter cooking. The sulphate is reduced to sulphide by organic matter during incineration as a step in recovery, and by its presence in the liquor subsequently made oxidation of the fiber is prevented, so that a good yield of strong fiber is obtained. The so called kraft papers are made by this process, which is not a popular one, as the gases formed have a very offensive odor, which affect the whole neighborhood of the mill and make the atmosphere almost unendurable to human beings, and incapable of supporting plant or vegetable life.

Some of the technical operations of the papermaker afford abundant opportunity for exercise of galenical ingenuity and skill as, for example, in the sizing of paper to give it a surface resistance to the penetration of liquids like ink, so that the paper may be written or printed on without the ink spreading over the sheet.

In the sizing of newsprint and the common grades of book paper the sizing substance is the ordinary rosin of commerce, which is added in the form of rosin soap to the pulp mass of fibers in the final stages of beating, and precipitated by alum, after the proper proportion of kaolin or china clay has been added (from 5 to 15 per cent) and the yellowish color of the ground wood has been toned up by the addition of sufficient blue and red aniline dyes or other colors required to impart a white appearance to the finished sheet of paper. In order to insure the perfect distribution of the rosin throughout the paper pulp it is introduced as a liquid soap, made by boiling rosin with soda ash and adding water, the following being a typical formula:

Rosin	1,350 lb.
Soda ash	165 lb.

Boil for about four hours and just before boiling is completed add about thirty gallons of water. Strain through a No. 80 sieve.

A definite quantity of the soapy emulsion of rosin thus formed is mixed with the contents of the beater, and when it is well distributed, alum is added in sufficient quantity to salt out the rosin and take with it for precipitation into the fibers of the paper pulp the kaolin and other ingredients of the furnish.

It is a disputed question in paper chemistry whether the alum simply throws the rosin out of solution, salts it out, as it were, or combines with it to some extent to form an aluminum resinate. The weight of authority leans to the conclusion that no chemical combination takes place, good results in sizing with rosin having been obtained by the substitution of magnesium sulphate, or diluted sulphuric acid, for alum. At best the salting out process as ordinarily practiced is not distinguished by scientific precision, and much more alum appears to be used than is necessary. Alum and rosin when present in excessive amounts cause paper to turn a brownish color, and it gradually becomes brittle and disintegrates in consequence of the formation of free acids and other chemical changes.

The supply of rosin is not inexhaustible and some scarcity has already developed, and as a consequence of this and a corresponding advance in price, the papermakers are casting about for cheaper substitutes. Besides experimenting with the waste rosins of the rubber industry, an attempt has been made to revive the ancient use of starch as a sizing material, with a fair measure of success as regards ordinary printing papers, but unsuccessfully in the case of writing papers, which require to be almost waterproof in their ink resistance. In this process a compound of starch and aluminum silicate is deposited in the fibers by combining in a cooking operation a partially gelatinized starch with sodium silicate and salting out the mixture with aluminum sulphate.

The more expensive handmade papers are sized with a solution of gelatine, the sheets being dipped separately into a tub of the size and afterward hung up to dry, being finally pressed between zinc plates. In another process now more generally used the sheets of paper are carried by traveling felts through a bath of heated size, the excess gelatin being removed by the action of rubber or wooden rollers through which the papers are passed before leaving the apparatus, and the drying is effected on an extension of the machine. With the ordinary machine made writing paper, however, the sizing material is mixed with the pulp in the beating engine, as in the case of newsprint and book paper, and there interlocked with the fibers by the alum salting out process previously described.

It is expected of the pharmacist that he should be well informed regarding methods of determining the quality of paper by microscopical and chemical tests at least—physical methods may be left to the experienced papermaker or dealer, who is often able to make a shrewd guess at the composition of a paper by the mere appearance and feel of the finished product.

In "taking the fiber count," as the method of estimating the proportion of pulps in a paper is termed, the use of a staining agent is necessary, all vegetable fibers being transparent and nearly colorless. The best stain for this purpose is Herzberg's chlorzinciodine solution, which is made up as follows:

SOLUTION "A."

Zinc chloride	20 Gm.
Distilled water	10 Cc.

Dissolve.

SOLUTION "B."

Potassium iodide	2.1 Gm.
Iodine crystals	0.1 Gm.
Distilled water	5.0 Cc.

Dissolve.

Dissolve "A" by adding the water to the zinc chloride in a beaker.

Dissolve "B" by adding a few drops of the water to the potassium iodide and iodine crystals in a glass beaker and after dissolving add the remainder of the 5 c.c. of water.

The two solutions—"A" and "B"—are then mixed together and allowed to stand for twenty-four hours to settle, after which the clear liquid may be poured off into amber glass bottles fitted with dropping stoppers.

A drop of Herzberg's stain applied to the paper pulp on a microscope slide brings out a wine-red color on cotton and linen fibers, gives a good clear blue color with bleached soda and sulphite woodpulps and a characteristic yellow or greenish gray yellow with ground or mechanical woodpulp.

The following method of preparing a sample of paper for the microscope is used by the Bureau of Standards, Washington, D. C.:

Several small pieces of paper of about the area of a cent are cut from different parts of the sheet of paper; these pieces are then placed in a beaker and covered with some ½ per cent caustic soda solution, and the whole mass is then brought to a boiling over a suitable heating device. After boiling for about a minute some tap water is added to wash out the caustic soda, followed by two or three drops of a 25 per cent solution of hydrochloric acid to neutralize the alkali.

The slightly acid solution is then poured off and enough of the small pieces of paper are pinched off and rolled into a ball of about the size of a pea. This small ball of pulp should be well rolled between the thumb and finger and then placed in a test tube and the test tube half filled with water. The test tube is then shaken vigorously until the paper has been entirely broken up and the fibers are well separated. A small portion of the pulp is then carefully removed on the point of the microscope needle from the test tube and placed on each end of one of the microscope slides, the excess liquid being removed by a pointed strip of filter paper brought in contact with the edge of the drop.

The fibers forming the pulp are thoroughly dried and a drop of the Herzberg stain is added, then the fibers are well "teased" out by the use of the microscope needles, a cover glass is placed over them and well pressed down, all the stain pressed out around the edges of the glass being removed with filter paper.

The slide is next placed under the microscope, and after studying the various fields an estimate of the proportion of each of the various kinds of fibers may be given.

One of the most frequently used solutions for staining fibers for microscopic examination is a solution of iodine in potassium iodide of the following composition:

Iodine	Gm. 1.15
Glycerin	Gm. 1.
Potassium iodide	Gm. 2.
Water	Gm. 20.

In contact with this solution cotten, linen, bleached hemp and ramie fibers are colored brown; while mechanical woodpulp, jute and manila hemp are colored yellow or yellow brown. Chemical pulp of wood, straw and esparto are not affected.

A solution of calcium nitrate in iodo-potassium iodide is said to offer some advantages over chlorzinc-iodine solution. For one thing it does not absorb moisture from the air and it does not alter the fibers. It is made as follows:

SOLUTION NO. 1.

Nitrate of calcium crystals	Gm. 100
Distilled water	Gm. 50

Dissolve.

SOLUTION NO. 2

Iodine	Gm. 1
Potassium iodide	Gm. 5
Distilled water	Gm. 90

Dissolve.

For use, 3 Cc. of Solution No. 1 is added to Solution No. 2.

This solution stains linen fiber a rose color, with a brownish tinge; ground wood is colored yellow; bleached sulphite fiber a delicate rose tint; unbleached sulphite fiber, clear yellow; soda popular fiber, indigo blue; straw fiber and esparto blue.

Several rough identity or diagnostic tests for the presence of ground wood in paper are employed by paper dealers, of which the following may be noted:

A solution of phloroglucin in alcohol is used for identifying mechanical or ground woodpulp, which turns a beautiful red color in contact with the reagent, the depth of tint, as compared with Schopper's standard color tables, corresponding to the amount of mechanical pulp, or lignified fiber, present. The procedure is as follows:

Into a flat porcelain dish pour two parts of a 2 per cent alcoholic solution of phloroglucin and one part of hydrochloric acid (phloroglucin, Gm. 1; alcohol, c.c. 50; hydrochloric acid, c.c. 25), and immerse in the solution the paper under examination. After ten minutes of contact compare the color developed with Schopper's standard color table.

In papers having a red or rose color the phloroglucin reaction breaks down and the employment of benzidine hydrochloride is recommended, this reagent giving rise to an orange color in the presence of mechanical woodpulp. The reagent is made by rubbing up 15 grains of chemically pure benzidine with 15 minims of hydrochloric acid and dissolving the benzidine hydrochloride formed in 2½ drachms of water at 122° F. The solution is simply dabbed on the paper to be tested, and the orange color produced in the presence of mechanical woodpulp is the more intensive the more woodpulp

is contained in the paper. The test is a very delicate one, the orange color being produced even when only traces of mechanical woodpulp are present.

Aniline sulphate stains lignified fiber yellow and a 10 per cent solution of this salt, acidulated with sulphuric acid, imparts a golden yellow tint to paper containing ground wood, the color being more or less intense according to the proportion of ground woodpulp present. A solution of aniline chloride and hydrochloric acid is also used, but the results with each of these aniline solutions are inferior to those obtained with phloroglucin.

Wuster's reagent is popular in Germany as a diagnostic test for ground woodpulp, but as it, as well as phloroglucin and the aniline salts, develop their characteristic colors with any lignified fiber, the test is not conclusive of the presence of ground woodpulp alone. Wurster's reagent consists of a 50 per cent solution of dimethylparaphenylenediamine in water. It gives a deep red color with ground woodpulp. There are now available test papers impregnated with Wurster's reagent which are called "di-paper" for convenience. Strips of this test paper are placed in a double sheet between the paper to be tested. After moistening the layers of paper with water the red color that develops is compared with a standard table of color values which is sold with the test papers.

It is the lignocelluloses, reacting to the foregoing reagents, which impart the greatest element of weakness and decay to paper. They are unsaturated compounds greedy of oxygen and profoundly affected by all oxidizing agents. Pure cellulose is a saturated compound which is resistant to the action of both chemicals and atmospheric changes, and this accounts for the practical indestructibility of rag papers, which are free from lignin and consist of nearly pure cellulose. Books and papers dating from the middle ages are to be found in museums and libraries today in a good state of preservation because they were made at a time when rags were the only crude material for the manufacture of paper.

The coal supply problem in Chile is receiving much attention in the country of late, and some of the coal-mining companies are seriously studying the matter of manufacturing briquets fro mthe waste or slack at the mines, said to average about 30 per cent of the total production, for the reason that the coal mined in Chile is so soft. A limited amount of briquets has been manufactured in this country during the past two years with good results, and now one of the leading coal companies in Chile (Compañia Carbinifera de los Rios de Cuarnilahue) has placed an order for a complete briquet plant, to cost about $95,000 United States gold, with a capacity of 250 tons each 10 hours. The average retail price of briquets is $10.10, gold, per ton.

TYPICAL AMERICAN USES OF CAST-IRON AND TEST METHODS APPLICABLE TO THEM.*

By JOHN JERMAIN PORTER, Staunton, Va.

American foundry practice has made great progress in passing from the empirical stage to that of scientific control. A most important feature, the use of chemical analysis as a basis for mixing irons, is now practically universally adopted, but much still remains to be done both in the more efficient use of chemistry and in the adoption of other scientific methods of control.

It is now becoming quite widely recognized that chemical composition is not the only factor determining the properties of cast-iron, but, although the importance of structure is known, the methods of metallography have received very little attention from foundries and users of castings. It is true that investigators have used the microscope on cast-iron with valuable results, but this method of control has not yet been generally taken up in practice, as in the case of steel. The two reasons which apparently account for this neglect are: First, the fact that foundries, being operated in smaller units, have as a rule less technical skill available at each individual plant; and, second, that the more complex structure of cast-iron makes the interpretation of its micostructure much more difficult. It is probable that much of the metallurgical progress of the near future will be along this line.

The theory that oxygen and nitrogen may be present in cast-iron and are accountable for some otherwise inexplainable phenomena is gaining ground among practical foundrymen, and means of eliminating these elements are being widely adopted. Greater care is being given the cupola process, and the use of ferromanganese, silicon, vanadium and titanium as deoxidizers is rapidly increasing. Ferro-alloys are also rather extensively used to correct the composition of the iron in the ladle.

Since cast-iron is used for a wide variety of purposes, it is obvious that the properties by which its value is measured and the tests to which it is subjected should be different for each class of castings. Hence it is necessary to consider each class separately. It is true that current practice does not as a rule adequately recognize this fact, and almost the only test which is commonly applied is that for transverse or tensile strength, although this property in many or perhaps the majority of cases is not of chief importance. There are but few foundries in this country devoting attention to getting special properties in this material, and to most foundrymen, as well as users, cast-iron is simply cast-iron, and a casting is satisfactory when true to pattern and free from visible defects.

*Paper presented at 6th Congress of International Association for Testing Materials, New York, 1912.

The succeeding portion of this paper will discuss some characteristic American uses of cast-iron, the properties needed, recent progress in meeting these needs, and the tests necessary to define the desired properties.

I. MACHINERY CASTINGS.

A large percentage of machine parts are made of cast-iron, which material is especially adapted for this use on account of the ease with which it is cast and machined into the desired shape. The more important properties desired in machinery castings are softness, strength, and a fine grain-structure, in addition, of course, to freedom from visible defects, such as blowholes, cracks, shrinkage cavities, etc.

It is an easy matter to make soft castings, but to get the combination of easy machining properties, strength, and close grain, as demanded by some users, has proved a difficult proposition to many foundries. Especially is this true as to closeness of grain and the ability to take a high polish, which is so desirable on many finished parts. The solution has been reached in various ways. The use of charcoal iron is one method, satisfactory except from the standpoint of cost. Certain brands of coke irons are found to give greater strength and closer grain for a given softness than others, and the knowledge of such mixtures is a valuable asset to the practical founder. Another method is found in the use of steel scrap in the cupola mixture, making the so-called semi-steel, which gives a closer grain-structure and considerably more strength without material change in composition. The treatment of the metal with certain ferro-alloys has also been found advantageous in this connection.

The buying of machinery castings would be greatly simplified if definite limits of hardness, strength, and grain size, could be specified. Satisfactory methods for testing hardness are found in the drill test and the Shore scleroscope, most of the various other proposed methods being too cumbersome for commercial use. The drill test, simulating as it does actual machining operations, gives the more reliable results, while the scleroscope possesses the advantage that it can be used directly on the casting without in any way injuring it.

For testing the strength of cast-iron there are available the ordinary transverse, tensile and compressive tests, the first of which is, in the opinion of the writer, preferable. In the testing of strength (and hardness also) it must be remembered that the properties of cast-iron depend in part upon the thickness of the section, and hence that, in cases where it is not possible to test the casting itself, the testpiece should at least approximate the section of the casting. Probably three standard sizes of test-bars could be selected, to represent the three classes of light, medium and heavy castings. The broken ends of these bars could be then used for the drill test to determine hardness.

For grain size there is no practical test available: a serious lack, as in many cases this property is of the greatest importance. Possibly something might be done with a planimeter used on a microphotograph of standard magnification; a rough test, of value in some cases, can be made by comparing the fracture of a broken test-bar with a scale made of previously broken test-bars of varying grain size.

The freedom from blowholes and other casting defects is best determined by ocular inspection. Unfortunately there is no method of inspecting the interior of the casting without destroying it, and while the tendency of the iron to shrinkage, blowholes, etc., can easily be tested, such tests would be of doubtful utility since these troubles are frequently, if not usually, due to faulty molding and pouring.

II. HYDRAULIC WORK.

Cast-iron is still very generally used for this class of work, on account of the ease with which it is formed into shape, although there has been some attempt to substitute steel for very high pressures. The properties desired in the metal are practically the same as in the preceding case, except that they stand in a different order of importance, close grain and freedom from shrink-holes and spongy places being the first consideration. Much the same means are used to obtain the combination of density, strength and the ability to machine easily, but as the importance of density is greater in this case, the use of special means, such as charcoal irons, steel scrap and ferro-alloys, is more frequent.

The most direct and satisfactory test for hydraulic work is to subject the casting itself to some specified hydraulic pressure. In many cases, however, the casting cannot be so tested until a good deal of expensive machine work has been done on it, and in this event it seems advisable to specify the strength and hardness tests previously described. The hardness test should be used in any case, as the bursting strength does not, of course, give any idea as to machining properties. A test for grain-structure would be especially valuable in connection with this class of work.

III. ELECTRICAL MACHINERY.

For parts where high electrical permeability is of prime importance, cast-iron has been largely displaced by steel, but in the majority of cases it still holds its own on account of the greater ease of forming. The permeabilty of cast-iron, although always low as compared with that of the purer forms of iron, can be considerably improved by keeping the manganese very low and the silicon quite high. In practice, however, not much attention is usually given to this property, since the greater number of castings are used in parts of machines not carrying the magnetic lines of force, and hence having requirements not different from ordinary machinery castings.

In electrical castings a permeability test used in conjunction with strength and hardness tests should be sufficient to define the quality of the material. Since permeability probably bears a fairly close relation to chemical composition it might be possible,

although certainly less satisfactory, to specify analysis in place of permeability direct.

IV. HEAT-RESISTANT AND CHEMICAL-RESISTANT CASTINGS.

A large variety of castings come under this head; the best known examples are probably ingot molds and grate bars. Only a few foundries are giving attention to producing castings of these special properties, and there is but little generally available information. Grate bars, for example, are ordinarily made of the cheapest possible mixture irrespective of its quality as regards service. In the case of ingot molds, on the other hand, some pains are taken to obtain the special quality of heat-resistance, and a low-phosphorus iron is always used for this purpose.

There are no tests for heat-resistance and chemical-resistance of cast-iron in common use. For heat-resistance it is a very difficult matter to devise any single test which will answer for all classes of castings, since the effects of heat are manifested in several different ways. Chemical analysis may be specified with advantage in some cases, since the melting-point of cast-iron depends chiefly on this factor. Resistance to the action of chemicals can be tested directly without much difficulty in a manner similar to the accelerated corrosion test used on steel. There is, however, great need for the standardization of all conditions under which such tests are made, so that comparable results may be obtained.

V. CHILLED CAST-IRON CAR WHEELS.

These form one of the most interesting applications of cast-iron in American practice. The service conditions for these wheels are very severe. The load on each wheel often amounts to between 10,000 and 20,000 lbs. They are constantly subjected to heavy blows due to ponding at rail joints. The friction of the brakeshoes induces severe heat strains in the tread. Finally the users of these wheels demand that they have a high resistance to wear. Owing to the nature of their service any failure is apt to be attended with very serious results, and hence great pains must be taken to insure a uniformly high quality of product.

The results desired are produced by the use of both special materials and special methods of casting. Formerly charcoal iron was used exclusively for this class of work, but now coke iron enters largely into the mixture. The problem of a high-grade mixture has been much complicated by the necessity of remelting the old wheels, with their usual high content of sulphur. A partial corrective for the excessive amount of scrap which it is often necessary to use is found in the addition of ferromanganese, and there have also been obtained some encouraging results through the use of ferrotitanium.

The special methods of casting consist in the use of a circular chill in that part of the mold forming the tread of the wheel. This method has been frequently described and needs no discussion. With the proper percentage of silicon this results in the tread being chilled to a depth of about ¾ in., back of which is tough gray iron. The chilled tread is, of course, intensely hard and exceedingly resistant to wear, while the wheel as a whole is very tough and has proven eminently satisfactory in service. Steel wheels, long used on passenger cars, have recently been substituted on freight cars of very high capacity. They are, however, much more expensive and in some cases have not proven entirely satisfactory as to wear, so that there is every indication that the cast-iron car wheel will hold its own for a long time to come.

The specifications and tests required for car wheels have been so often published and are so readily accessible that they need not be repeated at length. Briefly summarized the tests are carried out on a certain number of the castings themselves, and consist chiefly of a drop test to measure the resistance to shock and blows, a heat test made by pouring molten iron around the tread of the wheel, to measure the resistance to heat strains, and measurements to verify dimensions. It would appear that a hardness test on the chill might advantageously be added, in view of the known variation in the hardness of chilled iron. A test for wearing quality would be better still, but no satisfactory test of this sort is in sight.

VI. CHILLED ROLLS FOR ROLLING MILLS.

Cast-iron rolls still hold their own in sheet-mill and some other classes of finishing work, although cast-iron has been quite generally displaced by steel for the heavier service. In this case the service conditions are not unlike those to which car wheels are subjected, but they are even more severe as to heat strains. Moreover, owing to the great thickness of the castings the initial shrinkage strains are very great. The use of the very best grades of charcoal iron, together with air-furnace melting, is generally recognized as necessary for the successful manufacture of chilled rolls, chiefly on account of the difficulty with cracking due to heat strains. It is reported that the use of vanadium in chilled rolls is adding considerably to their wearing qualities.

For this class of castings there are no satisfactory tests in sight. It is inconceivable that any tests could be of value which are not made on the roll itself, and, while a difficult proposition, it is possible that in time a set of tests similar to those used on car wheels may be devised.

VII. BRAKESHOES.

Brakeshoes may serve as an example of the many smaller specialties which are made of cast-iron. The requirements here are long life, with this limitation: that the hardness of the brakeshoe must be less than that of the wheel, so that the wear will not be on the wheel. A close grain-structure is advisable, and in some cases at least is being obtained by the use of steel scrap in the cupola mixture.

For brakeshoes a wearing test used in connection with hardness limits would best define their quality. No satisfactory method of testing resistance to wear

is in sight, but it would seem that specifications for hardness alone could be advantageously used pending the development of such a test.

VIII. CAST-IRON PIPE.

In point of tonnage, pipes are probably the most important castings made in this country. Cast-iron is a particularly suitable material for pipes which are to be placed underground, on account of its relative resistance to corrosion as compared with steel and other commercially available materials. Competition is keen in this line, so that low-priced iron is necessary. Within the limitations set by price, close grain and strength are desirable, while hardness must be kept within such limits as will permit of a small amount of machine work.

In regard to the properties of the metal, none of the present specifications for cast-iron pipe lay stress on anything other than strength as determined on a separately cast test-bar. A test for bursting strength and freedom from leakage made directly on the pipe would, of course, be a more accurate index of utility, but is probably too cumbersome for practical use. The transverse-strength determination is probably as satisfactory as any simple test could be, but might with advantage be supplemented by specifying hardness limits.

IX. STOVES AND FURNACE WORK.

Malleable cast-iron and steel have been tried for stoves, but while they have perhaps a place, gray cast-iron has proved more satisfactory and has steadfastly held its own. The service requirements here are resistance to the action of heat, resistance to warping, and a certain degree of strength. However, as these castings are very thin and are frequently highly ornamented, a very fluid iron is essential, and in practice the service requirements are deliberately ignored to facilitate manufacture. Resistance to heat requires low phosphorus, and resistance to permanent expansion, which causes warping, demands low silicon, but both phosphorus and silicon are invariably carried high in this class of work, to increase fluidity and make it easier to produce perfect castings. However, the product of our stove foundries is fairly satisfactory in service, and in appearance and finish has reached a high degree of perfection.

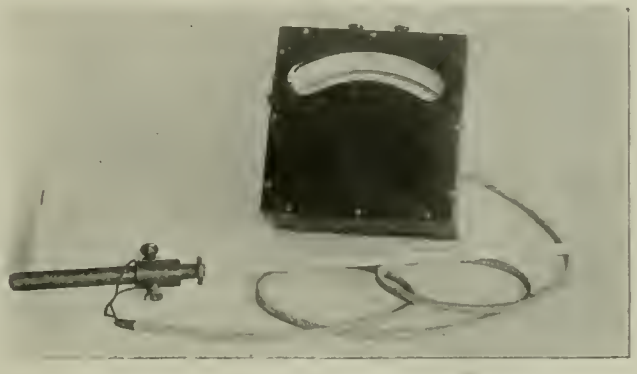
Specifications for stove and furnace castings should include tests for strength, hardness (since many parts have to be drilled), and resistance to heat. There is no trouble in regard to the first two tests, but, as previously stated, no good method has yet been devised for gaging heating-resistant qualities. Specification of chemical analysis can be used with advantage, but cannot be regarded as a really satisfactory substitute for the much-needed direct test for heat-resistance.

There are, of course, innumerable other uses of cast-iron which might be described, but to make the catalog complete would be an interminable task. In conclusion, the fact should be emphasized that in many cases it is not possible to do much in the way of formulating specifications on account of the lack of suitable methods of testing the properties. The apparent inclination of many users of castings to entirely ignore the quality of their material may be largely attributed to the lack of any definite numerical means of gaging quality.

AN ENGLISH THERMO-ELECTRIC PYROMETER.

By FRANK C. PERKINS.

It is held that in using the English-thermo-electric pyrometer shown in the accompanying illustration no calculations are necessary. It is used for ascertaining



View of Thermo-Electric Pyrometer.

the temperature of high speed steel furnaces, case-hardening furnaces and steel castings as well as annealing open-hearth furnaces and glass furnaces. The thermo-electric pyrometer indicates any temperature up to 1600 C., the temperature being read off direct.

The principle of instrument is simple as the pyrometer only consists essentially of a thermo junction of two dissimilar metals which heated produce an electric current. The thermo-junction is enclosed is a silica tube, and the other end of the metals is connected up by means of electrical leads of any length with a specially constructed, delicate Nivoc moving coil direct reading indicator.

It is held that one of the great advantages of this indicator is that when fixed in the works or foreman's office and a number of thermo junctions connected up with same by means of a switch, the readings of several furnaces are systematically taken. In this English instrument pivot suspension entirely dispenses with the trouble due to breakage of the phosphor-bronze strip, as in the older form of instruments. One indicator can be arranged to control a number of furnaces, and no batteries are required, while no special skill is necessary in manipulation.

The thermo-couples are standardized, and accuracy is obtained within one point in a hundred. It will be seen that no leveling is necessary, and vibration in the workshop does not interfere with the accuracy. The indicator, being of the moving coil type, is not

influenced by external electric or magnetic current. The total resistance of the instrument is about 100 ohms, thus allowing the resistance of the connections to the couple to be neglected, even when the indicator and couple are many yards apart. The thermo-couple is inserted in the furnace through a hole, either in the side or end of same, but in the case of open galvanizing baths it may be bent in the hand and inserted in a vertical position. It is held that the insertion of an inch is ample. The steel sheath is renewed when burnt away to about one-third of its original thickness, but this is inexpensive and easily fixed. Care is exercised in removing the sheath from the inner tube, as the latter is somewhat brittle. The same thermo-couple can be used in any number of furnaces, provided they are reasonably close together, by suitable wiring, the circuit being broken opposite each furnace, the thermo-couple being simply connected to terminals placed at each break.

RECOVERY OF CELLULOSE FROM ASPARAGUS.*

The invention of the much-discussed process for the recovery of cellulose from asparagus waste from canning factories and from asparagus stalks that mature after the edible crop has been gathered is due to Prof. Otto Reinke, whose communication on this subject to the Institute for Chemical Technology at Brunswick is as follows:

For several years I have caused my employes to make tests concerning improvements in the use of waste in the agricultural-chemical trade, and through these tests interesting results have been reached as to combinations of nitrogen (more especially fermented) and hydrates of carbon (more especially cellulose). It was found practicable to manufacture, with excellent success, both as to quality and quantity, pure cellulose from asparagus waste (German patent "Anm. R." 36,808).

The asparagus pulp waste, which represents up to 30 per cent of the whole asparagus stalk, and which decomposes very quickly on account of the high contents of water and asparagin, sours easily, has only a comparatively small value and low nutritive qualities as fodder, and must often be used as fertilizer when coming from the vegetable-canning factories. Attempts have been made to dry small quantities for use in place of excelsior for packing purposes (the price obtained for it amounted to $0.48 per 110 lbs.), but this can be disposed of only in small quantities, as it decomposes more readily than excelsior. There was also an attempt to manufacture crude packing paper in a mechanical way, but without success. The plant is allowed to grow on the fields until November (in Brunswick up to Dec. 15), and must then be removed and burned on account of the fungous parasites that are injurious to the asparagus fields.

If soup extracts are manufactured from the boiled freshly washed asparagus pulp, it is an easy task to obtain a pure cellulose mass by a chemical method. The supply of the plant that is allowed to grow after the edible stalks have been removed is greater and, after being cut in small pieces like chopped straw, such as is used in the manufacture of straw paper (if asparagus pulp is used it is scarcely necessary to chop it), it is treated with sulphurous acid, or, better, with 8 to 12 per cent lye of soda (Na_2O), in steam-tight vessels at 4 to 6 atmospheres for 1 to 3 hours. The result is a heavy brown solution of cellulosine, the incrusting substance, and of lignin, the albuminous substance, and in addition thoroughly disclosed cellulose in both short and long fiber from, in long drawn cells, and frequently in final spiral form. According to the cutting by machinery different qualities of cellulose may be manufactured. The result is often a beautiful pure cellulose product, and after the material has been washed and treated with oxidizing and reducing substances, for example, with diluted solutions of permanganate and sulphurous acid, it may be used for bandages, blasting material, paper, tissues, fine felt, cardboard, etc. If pulp and plant are supplied free by the large factories and directly from the fields, respectively, or even if it is necessary to pay a trifle for these supplies, it is easy enough with a very small plant, either in connection with some vegetable-canning factory or in a separate establishment, to carry on a periodical work in the asparagus districts.

One acre of asparagus land will furnish 2,849 lbs. of asparagus (after deducting 20 per cent for fresh asparagus used and shipped in original state) and yield about 667 lbs. of pulp or 80 lbs. of dry substance, equal to 12 lbs. of cellulose. One acre of asparagus land also furnishes, on an average, 1,958 lbs. of plant or aftergrowth, or 1,602 lbs. of dry substance, which will make 176 lbs. of cellulose.

It is necessary that the outer-skin cell groups, fiber strands, and pieces of tissue attached to each other be perfectly separated and, if necessary, sorted into different qualities.

*Consul General Robert P. Skinner, Hamburg, in the Daily Consular and Trade Reports.

According to the *American City* Germany has satisfactorily demonstrated that it is possible to light towns by sewage gas at a profit. The municipality of Bruenn, after many years of experiment, has perfected machinery which dries the sewage and afterwards distills it in retorts, in the same way as gas is distilled. In two and one-half hours' distillation 100 kilogrammes of sewage mud yield 23.8 cubic kilometers of gas of virtually the same composition as coal gas. In addition are obtained good coke and three times as much ammonia as is given by an equal weight of coal. The profit is so great that it is said to cover the whole cost of running the municipal sewage purification works, in addition to solving the problem of disposing of sewage in an absolutely hygienic way.

METHOD OF ANALYSIS USED IN THE LABORATORIES OF THE ARMOUR INSTITUTE OF TECHNOLOGY.

Gas Analysis.

(A) HEMPEL APPARATUS.

The gas is measured in an accurately graduated pipette connected to a leveling bottle and the volume is always read at atmospheric pressure or in other words when the water level in the bottle is the same as the water level in the pipette. In this apparatus, the gas is discharged into a second pipette containing a reagent which dissolves one constituent. The gas is drawn back into the original container and measured. The loss gives the desired constituent and since the original volume is 100 cc., is read directly in per cent. The greatest error in gas analysis is due to change in temperature of the gas. The measuring pipette is water-jacketed, and if allowed to stand at room temperature and if sufficient time be allowed before each reading, the error becomes almost negligible.

The gas sample is taken either from a gas hose direct or from a gas sample tube. In the latter case, the gas should be forced into the pipette by displacement with water. All air should be removed from the connecting rubber tubes by filling with water. All joints must be absolutely gas tight.

The volume of the sample taken should be within .2 cc. of 100. This may be obtained by running in the gas slowly and measuring each addition with the leveling bulb or by running in slightly over the 100 mark, removing the supply hose and forcing the gas out by the leveling bottle till the exact mark is reached. The sample should be allowed to stand a few minutes before the exact reading is made.

Connection is made to the capillary end of the pipette containing the solution by means of a U-tube of capillary glass. The second pipette is held on a convenient stand so that the top of the tube is at the same level as the top of the measuring pipette. The U-tube is connected to the absorption pipette by pure gum tubing with the glass ends together, the solution is blown up into the U-tube and held there while the glass end of the U-tube is placed against the top of the measuring pipette and a piece of pure gum tubing slipped over. The object of this procedure is to prevent excess air in the capillary. The point at which the solution stands in the capillary is marked, the gas forced into the absorption chamber by opening the valve and raising the leveling bottle until all the gas is over and the capillary filled with water. The pipette is shaken intermittently for 2 to 3 minutes and the gas passed back until the absorbing liquid stands at the same point in the capillary as it did when starting. After standing two minutes the gas volume is read.

The first determination which is seldom made, is for benzine vapors. The absorbent is absolute alcohol, after which a pipette of water should be used to remove the alcohol vapors. This water should be previously saturated with the gas to be analyzed, or serious error may result.

The next, which is usually the first determination is for CO_2. The absorbent is 50 per cent KOH, usually made from commercial caustic, filtered through hardened filter paper. In some of the Hempel pipettes there is a bulb of glass beads to break up the gas. With these, it is advisable to run the gas back and forth as well as shake the pipette.

Illuminants or heavy hydrocarbons are determined next. The absorbent is fuming sulphuric acid or strong bromine water. The acid must be very fresh and must not come in contact with the rubber, as considerable gas is evolved. With either liquid, the KOH bulb must be used before the gas volume is read, to absorb the vapors of the solutions.

Oxygen is next absorbed in strong potassium pyrogallate, made by adding 5 per cent solid pyro-gallic acid to 50 per cent KOH. This solution must be fresh and will not keep long even in a double pipette with a guard solution to keep the air from it. Small sticks of yellow phosphorus in water are sometimes used, but are apt to change to the red variety on long standing, so the fresh pyro-gallate is the safest.

The next in order is carbon monoxide, which is absorbed in cuprous chloride, made by allowing hydrochloric acid (strong) to stand on excess copper. This solution must also be kept in a double pipette and two pipettes should be used for absorption. The CO forms an addition product with CuCl, which readily gives off the CO. Hence a complete absorption in one pipette is almost impossible, and a second one with fresh solution should be used for the final absorption.

The remaining gas is allowed to escape down to 15 cc., or if a containing pipette is at hand, it may be saved for a duplicate explosion. To the gas residue, oxygen or air, or both are added to form an explosive mixture. For ordinary illuminating gas, 50 cc. air and 10 cc. oxygen or 70 cc. air form a good mixture. For producer gas, the entire residue from the CO is used with 15 to 20 cc. oxygen. The volume after the admission of the oxygen is read carefully. The mixture is run over into the mercury pipette which is

closed off by a pinch clamp. The gas is placed under reduced pressure by lowering the mercury leveling bulb, and exploded by passing a spark from an induction coil across the platinum terminals in the pipette. The spark should only be on for an instant, as the nitrogen will oxidize rapidly. If the gas does not explode, the mixture is wrong, and it is sometimes necessary to add a few cc. of pure hydrogen to obtain a proper explosion from very lean gases. This, of course, is deducted later. After the explosion, the gas is passed back into the measuring pipette, allowed to stand at least five minutes, and the volume noted. The CO_2 formed by the explosion is absorbed in the KOH pipette and its volume noted.

The following is a typical calculation of the hydrogen and methane:

Let volume after CO	= 60.0 cc.
Volume used	= 15.0 cc.
Diluted with air to	85.0 cc.
Volume after explosion	= 69.0 cc.
CO_2 absorbed after explosion	= 5.0 cc.

Then since methane forms an equal volume of CO_2,

$$\text{per cent methane} = 5.0 \times \frac{60.0}{15.0} = 20.0 \text{ per cent.}$$

Since methane unites with two volumes of oxygen to form one volume of CO_2, the contraction due to the explosion of the methane is $5 \times 2 = 10$ cc.

Since the total contraction on explosion is $85 - 69 = 16$ cc., the contraction due to hydrogen is $16 - 10 = 6.0$ cc.

Since two volumes of hydrogen unite with one volume of oxygen, the amount of hydrogen present in the explosion is $6.0 \times \frac{2}{3} = 4.0$ cc. Therefore the per cent hydrogen in the original gas is $4.0 \times \frac{60}{15} = 60.0$ per cent.

The difference between all the gases found and 100 is assumed to be nitrogen.

(B) MOREHEAD APPARATUS.

The Morehead apparatus differs from the Hempel in that the absorbents are run through the gas instead of the gas into the absorbent. The sample is drawn into the water jacketed graduated burette in an exactly similar manner to the Hempel apparatus except that there is a side opening which may be used by means of the 3-way stop cock. The "bell" at the top of the pipette is filled with 50 per cent KOH or any absorbing solution, the leveling bottle is closed off from the pipette by turning a three-way stop cock at the bottom. This connects the pipette to a water seal at the bottom. The solution is allowed to trickle slowly down the sides of the burette and absorb completely the desired constituent. The excess runs out into the water seal which should be kept at nearly a constant maximum level by a suction pump. The absorbing solution should be washed out completely by water after the absorption is complete. The wash water is preferably saturated with the gas to be analyzed as fresh wash water absorbs small amounts of the gas. The time required for an absorption should be at least three minutes or more, especially with CuCl solution. When the gas is thoroughly washed the water seal is disconnected, the leveling bulb reconnected, and the gas volume read. About two minutes should be allowed for equalization of temperature.

The solutions used are the same as in the Hempel apparatus, except that bromine (three drops in a bell full of water) is always used for illuminants, and pyrogallate (made immediately before use) for the oxygen. It is necessary to absorb the bromine vapors with a little KOH before reading the contraction due to the absorption of illuminants. After the CO determination, the excess gas is held in a special reservoir at the top, displacing the water with which it should be filled. Careful manipulation of the three-way stop cocks is necessary to obtain accurate results, also entire absence of air bubbles. The explosion should be duplicated with this excess gas as the large factors employed in calculation multiply a small error. The dilution, explosion, absorption of CO_2 and calculation are exactly the same as employed for the Hempel apparatus.

Other tests frequently employed are those for H_2S and total sulphur. The method for the former is usually only qualitative; the gas is passed over strips of paper in a glass jar moistened with 6.5 per cent solution of lead acetate. Any coloration (dark brown or black) shows H_2S. A fairly quantitative test may be made by bubbling a known quantity of gas through KOH (25 per cent)or $CdSO_4$, diluting to large bulk, making strongly acid with HCl and titrating with standard iodine. The sulphur may be readily calculated. Another method employs bromine water. The excess bromine is boiled off at the end of the passage of gas, the solution made acid with HCl, and the sulphur precipitated as $BaSO_4$ in the usual manner.

The total sulphur may be determined by burning a known quantity of the gas with ammonium sesquicarbonate in a specially designed apparatus to condense or absorb the products of combustion. The solution at the end of the run is washed out of the container, made acid with HCl and the total sulphur precipitated with excess $BaCl_2$.

The calorific value of the gas is best determined in a calorimeter of the Junper type such as the Junper itself or the Sargent Automatic Gas calorimeter. The principle involved is that if gas is burned at a constant rate inside of a properly designed calorimeter cooled by a constant supply of water at a constant temperature, the water will be raised in temperature a definite amount. If gas volume, weight of water and elevation in temperature are very uniform and accurately measured, the heating value of the gas may be accurately calculated.

The circulating water is first turned on and a constant head maintained by the special overflow tank at-

tached to the calorimeter. The burner is lit and the rate of flow adjusted so that within less than 1 per cent of 5 cubic feet per hour pass through the meter. The temperatures of the incoming and outgoing water are read at intervals and when they become constant, and the water of combustion is dropping regularly from the drip tube, the run is started. The cooling water is run into a weighed tank, the thermometers on incoming and outgoing water and gas are read at regular intervals, two to three minutes apart. The pressure of the gas at the meter is noted regularly, and the volume of gas, weight of cooling water and volume of drip (in cc.) are noted for the entire run which may be a half hour or longer. The barometer reading should also be taken.

The apparent volume of the gas from the meter is calculated to 62° F. and 29.92 inches of mercury. The total heat this gas gives out is formed by multiplying the weight of cooling water by its average rise in temperature. If the outgoing gas is at a different temperature from the incoming, a correction of .25 B.t.u. per degree difference in temperature per cubic foot should be applied. This gives the total heat of the gas. The effectual heat is obtained by subtracting the heat due to the condensation and cooling of the water of combustion. This may be calculated from the steam tables, but a convenient factor is cc. $\times$ 2.5 = B. t. u. This is subtracted from the total to give the effective B. t. u. per cubic foot.

The gas calorimeter may be checked against the gas analysis or the heat valve of the gas calculated from the analysis by use of the following factors:

Per cent CO	$\times$ 3.44	= B. t. u. per cu. ft.
Per cent illuminants	$\times$ 17.28	= B. t. u. per cu. ft.
Per cent hydrogen	$\times$ 2.935	= B. t. u. per cu. ft.
Per cent methane	$\times$ 9.66	= B. t. u. per cu. ft.

Total B. t. u. per cu. ft. sum of above.

We find that the B. t. u. as calculated from the gas analysis checks pretty closely with the B. t. u. as determined in the gas calorimeter. The variation is usually less than one per cent, even on gases of low B. t. u.

According to the Manchester (England) Guardian, Belgium appears to be the only country where the manufacture of artificial silk by the old guncotton process still yields handsome profits. This appears to be due to the fact that alcohol and ether are obtainable there much more cheaply than elsewhere. The report of the Fabrique de Soie Artificielle de Tubize, the large Belgian producers, discloses $458,240 net profit. The total capital is $700,000. It would appear that the competition of the newer processes is regarded seriously by the company, for $193,000 is set aside from the profit available in order to purchase the Belgian patent rights for a new method. No specific mention is made in the report as to what the process in question is, but it is understood to be a viscose one.

DETERMINATION OF HYDROGEN, NITROGEN AND METHANE IN GAS BY COMBUSTION IN A QUARTZ TUBE.*

By PROF. MATHERS and MR. IRA E. LEE.

The purpose of this research was to devise a more convenient and a more accurate method for the determination of hydrogen, nitrogen and methane in gas. Many different methods have been advocated for making this analysis.[1] The combustion of these gases by explosion with oxygen in an explosion pipette was the method generally used until a few years ago. Results with this method in this laboratory have been very unsatisfactory. The difficulty has been that the gases were not completely burned. This gives a result for nitrogen which is too high and causes the gas to appear worse than it is.

A much better method employes the Winkler-Dennis pipette, in which the gas residue is treated with an excess of oxygen in the presence of a platinum spiral which is heated to redness by a current of electricity. This method, we think, gives accurate results when all of the conditions are favorable. The great difficulty is in fastening the spiral in such a way that no metal except platinum is exposed to the action of the hot oxygen. Base metals such as iron are readily oxidized by the oxygen. This introduces a serious error into the work. If the platinum wire for electrically connecting the coil is sealed through glass at a point near the heating coil, the glass at the joint is almost certain to crack. In most forms of the apparatus, the platinum spiral is fastened to stout iron wires which are inclosed in glass tubes. These tubes enter the pipette through holes in a rubber stopper. A cement is used to make the iron wires in the glass tubes gas tight. This form of apparatus would be satisfactory if platinum wires were used in the place of the iron wires, but this is too expensive. The ends of the iron wires in the pipette are oxidized during each combustion. This error increases the percentage of hydrogen and lowers the percentage of nitrogen. A modification of the apparatus, as devised in this laboratory, overcomes these objections and difficulties. Two short pieces of platinum wire were sealed into the ends of two glass tubes. The platinum spiral which was to be heated was fastened to two platinum wires, which were then thrust in the open ends of the glass tubes. These wires extending into the glass tubes were bent into wavy shapes, so that they would be held in position by contact with the sides of the tubes. When the pipette was filled with mercury, these glass tubes were filled (and remained filled) with the mercury, so that the electrical connection was complete from the outside platinum terminals through the platinum spiral. The places where the platinum wires were sealed in the glass were so far from the

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[1] "Review of Progress in Gas Analysis," Chemiker Zeitung, 32, 801 and 817 (1908).

heated spiral that there was no trouble with cracking. A platinum spiral, made by twisting together several very small platinum wires, lasts much longer than a spiral made of a single platinum wire. The spiral must be smaller in diameter than any of the other pieces of platinum which are used. This apparatus gives correct results when properly manipulated.

One source of error is always present in all combustion over mercury. If the spiral is heated too hot, the mercury is oxidized, while if the temperature is so low that there is no danger of oxidizing the mercury, the combustion of the gases will be incomplete. The Drehschmidt method[2] avoids this error, since no mercury is present during the combustion. This method of burning the gas residue mixed with oxygen, by passing it through a hot platinum capillary tube, is perhaps the best scheme. However, the high cost of the platinum capillary tube, together with the rapid deterioration of the apparatus, makes a modification desirable. The experiments described in this paper show that the quartz tube filled with pieces of scrap platinum is an entirely satisfactory substitute for the platinum capillary tube in the Drehschmidt apparatus.

The quartz tube was 30.5 cm. long, 7.25 mm. outside, and 3.38 mm. inside diameter. Its volume, determined by the weight of mercury required to fill it, was 3.317 cc. The platinum scrap, which was used as a contact substance in the quartz tube, was prepared by cutting pieces of ordinary scrap platinum wire, which every laboratory has in quantity, into as short pieces as possible with shears. These small fragments were then placed upon stiff paper which passed through a cornet roll mill a number of times. These flattened pieces of platinum presented a large surface to the passing gas, and at the same time offered very little resistance to the passage of the gas. Two pieces of scrap platinum gauze were used, one in each end of the quartz tube, to keep the small pieces of platinum in position. The platinum weighed 11,189 grams, and had a volume of 0.522 cc. The platinum occupied 21.6 cm. of the length of the tube.

The data concerning the many preliminary experiments, which merely served to detect the errors, will be omitted. The following form of apparatus and manipulation were found satisfactory:

A mercury pipette, holding the gas to be burned and the oxygen required for the combustion, was connected to one end of the quartz tube by a suitable capillary tube with rubber connections. A mercury burette, arranged to receive the gas, was connected to the other end of the quartz tube in a similar manner. Pinch-cocks, one on the burette and one on the pipette, controlled the connections with the quartz tube. The burette was provided with a water jacket, which was connected at its lower end with a level bottle, so arranged that the water could be drawn out and then passed back into the water jacket. This circulation and thorough mixing of the water were necessary to prevent unequal temperatures between the top and bottom of the burette. The water jacket was improvised from the outside part of a Liebig condenser. A thermometer, which showed the temperature to the water and gas, was suspended about midway of the burette inside of the water jacket. The quartz tube was heated by a bunsen burner provided with a wing tip which produced a broad flame. An asbestos board was suspended about 5 mm. above the quartz tube, to lessen the radiation of heat. The manipulation was: The temperature of the gas in the pipette—that is, the temperature at which it was measured—was carefully read. The pinch-cock connecting the burette to the quartz tube was opened and the burner was lighted for 3 minutes. The increase in volume of the air in the quartz tube produced by the heat was cared for in the burette. The pinch-cock connecting the pipette to the quartz tube was opened and the level bottle was raised so that the gas and oxygen passed slowly and regularly over the glowing platinum, generally about 3 minutes being required. In no case was there any indication of an explosion in the pipette, even when the velocity of the gas was greatly increased. The level tube on the burette was raised and the level bottle on the pipette was lowered so that the gas was forced back from the burette into the pipette. The gas was then again passed through the quartz tube over the glowing platinum into the burette. The flame and the asbestos board were removed and water was poured upon the quartz tube to cool it. After the quartz tube had reached room temperature, the pinch-cock connecting the burette and quartz tube was closed. The mercury in the burette and level tube was leveled. The water in the water jacket was passed back and forth by means of the level bottle until the thermometer in the water jacket showed constant temperature. The mercury in the burette and level tube was again carefully leveled and the volume of gas was read. The final gas volume was always corrected for variation from the initial temperature.

The process as described above was tried with pure hydrogen gas, which was prepared by the action of boiled dilute sulphuric acid upon pieces of zinc contained in a gas double pipette for solids. The pipette was filled with boiled distilled water to displace the air. The sulphuric acid was added through a glass tube which entered through the opening for the introduction of solids into the pipette. The hydrogen gas was allowed to escape completely from the apparatus several times before any was saved for analysis. This form of generator very effectively protected the hydrogen gas from the diffusion of air. The results are given in the following table:

Hydrogen used.	Air added.	Volume after combustion.	Time of experiment, minutes.	Total experimental.	Contraction theory.
26.02	90.6	77.6	2.5	39.03	39.03
21.06	77.9	66.75	2.3	31.6	31.59
20.4	77.9	67.7	3.5	30.6	30.6

[2] Hempel-Dennis, "Gas Analysis," page 140.

The following table shows the results which were obtained in the analysis of gas residues:

Residue cc.	Oxygen cc.	Volume after combustion.	Time.	Total contraction.	Carbon dioxide.	Hydrogen.	Nitrogen.
51.9	80.4	50.2	.	82.1	18.8	28.4	4.7
52.3	71.3	42.4	3	81.4	17.5	29.4	4.25
58.73	67.18	38.0	2	81.34	17.77	29.0	3.9

The result in experiment 1 was obtained with the ordinary combustion pipette. This value was taken as the standard. Experiment 2 in the table shows 17.5 per cent of carbon dioxide, which was, of course, obtained by the absorption of the carbon dioxide which was in the burette. This value must be corrected for the amount of carbon dioxide which remained in the quartz tube. The total gas residue after combustion (including the air originally in the quartz tube) was 42.4 plus 2.795 (the volume of the quartz tube which was unoccupied by platinum), which was 45.195. So, 93.8 (42.4 — 45.195) was the per cent of the gas which was measured in the burette. The carbon dioxide in all the gas after the combustion was 17.5 — 93.8, or 18.65 per cent. All carbon dioxide readings were corrected in this manner. The variations of the results in experiments 2 and 3 from the standard in experiment 1 are small and perhaps due to changes in the gas, since the three experiments were made on three successive dates. To avoid this variation from day to day, several gas residues were prepared for analysis one afternoon, were mixed in a water pipette and portions of this mixture were used for analysis. The results are:

Residue.	Oxygen.	Volume after combustion.	Time.	Total contraction.	Carbon dioxide.	Hydrogen.	Nitrogen.	Methane.
49.92	68.8	41.5	2.0	77.22	18.65	26.6	4.69	18.65
49.95	68.9	41.55	3.5	77.3	17.45	26.65	4.64	18.66
49.90	68.9	41.6	3.5	77.2	17.6	26.5	4.7	18.70

All of the results given in the tables show that the quartz tube is as accurate as the combustion pipette. It was found necessary to pass air through the quartz tube to remove the carbon dioxide produced by one experiment if another experiment were to be made at once. If only total contraction was desired, the carbon dioxide did not need to be removed. If nitrogen was to be determined, the gas remaining in the tube from previous experiment had to be removed by passng air.

This apparatus gave an excellent method of determining the total nitrogen in gas. The gas was mixed with an excess of oxygen whose nitrogen content was accurately determined. After combustion in the quartz tube, the gas was passed into potassium hydroxide to take up the carbon dioxide, and alkaline pyrogallol to take up the excess of oxygen. The unabsorbed residues consisted of the nitrogen in the gas and the nitrogen which was in the oxygen. The results are as follows:

Gas.	Oxygen.	Nitrogen added in oxygen.	Total nitrogen.	Nitrogen in gas taken.	Nitrogen per cent in gas.
49.9	76.4	7.10	8.68	1.58	3.17
50.0	74.05	6.95	8.62	1.67	3.34
49.93	78.04	7.19	8.78	1.59	3.20

Other tests showed that under the conditions of the experiment less than 67.7 of the oxygen (63.4 cc. of pure oxygen) did not give complete combustion with 50 cc. of the gas. This was 12 cc. of pure oxygen in excess.

Since the work which is described in this paper was completed, Hempel, a German authority on gas analysis, has published the same method, except that he heated the quartz tube with a blast lamp. He also described an arrangement for heating a platinum spiral inside a quartz tube with electricity. Electrical connections were made by sealing platinum wires into glass capillary tubes, which were then attached to the quartz tube by rubber tubing. Hempel says that the older methods of burning the gas were never accurate because the temperature of the platinum spiral was never high enough. He thinks that these methods which use the quartz tubes (or the platinum capillary) are the only ones which give accurate results.

After considering all of these results, one feels that the older methods of determining hydrogen, nitrogen and methane are about to be supplanted by a new and more accurate method.

Summary.—Gas residues, after the addition of oxygen gas, were burned by passing them through a heated quartz tube which contained pieces of scrap platinum. The results are very accurate. The advantages of this apparatus over the standard combustion pipettes are:

1. The quartz tube and pieces of platinum are not easily broken or damaged during use. The quartz tube is brittle, but will break only if struck a blow. The combustion pipette is very easily broken, and the small platinum wire often burns out, even when great care is exercised by the operator.

2. No metal or other substance which can be oxidized or acted upon by any of the gases is present in the quartz tube during the burning. In the combustion pipette, mercury, an oxidizable metal, is always present. In some of the experiments during the research, the conditions were such that very serious errors were made by the absorption of gases by the mercury. Everyone is familiar with the formation of oxides upon the mercury and upon the sides of the combustion pipette.

3. Small cracks in glass tubes, or leaks around the rubber stopper or places where glass tubes enter in the combustion pipettes, cause serious errors. There is very little chance for leaks in the quartz tube apparatus.

4. Platinum scrap, such as short lengths of wire, which we generally find plentiful in laboratories, is used in this apparatus. The quartz tubes are cheap.

5. The temperature in the quartz tube may be made high enough to insure complete combustion of the gases.

The disadvantages of this new process are:

1. The gas becomes heated during the combustion, so care must be taken to determine the final temperature at which the gas is measured. Corrections must be made for all temperature changes.

2. A correction must be made for the carbon dioxide which remains in the quartz tube after the combustion. This disadvantage can be overcome, perhaps, by the use of a smaller bore capillary quartz tube, in which the volume is so small that a correction is unnecessary.

THE PRESENT CONDITION OF THE MECHANICAL TESTING OF INDIA RUBBER ACCORDING TO THE EXPERIENCE GAINED FROM THE EXPERIMENTS CONDUCTED AT THE ROYAL LABORATORY FOR TESTING MATERIALS, BERLIN-LICHTERFELDE, W.*

By PROF. K. MEMMLER, Berlin-Lichterfelde, W.

A report (Nr. XV$_2$) was laid before the V Congress (Copenhagen) by Memmler and Schob, on the results of an extensive work carried out at the Gross-Lichterfelde Laboratory and relating to tensile tests with annular and rod-shaped test pieces of soft rubber of different kinds. The full report on this work was published in the "Mitteilungen aus dem königl. Materialprüfungsamte," 1909. Part IV, under the title: Beiträge zur Frage der mechanischen Prüfung von Weichgummi. I. Über den Einflus der Probeform auf die Festigkeitsergebnisse, von K. Memmler und A. Schob (Contributions to the question of the mechanical testing of soft rubber. I. On the influence of the shape of the test piece on the tinsile strength) and was also laid before Section C of the Congress. The present brief report on the condition of the mechanical testing of rubber is based principally on the experience gained in the Gross-Lichterfelde Laboratory since 1909. An exhaustive critical review of the literature on the mechanical testing of rubber up to 1910 has been given by the author in his work, written in collaboration with Prof. Hinrichsen, "Der Kautschuk und seine Prüfung" (Rubber and the Testing of Same)—published by S. Hirzel, Leipzig 1910—so that it would be superflous to touch upon the earlier work at present.

Since the date of the Copenhagen Congress, the experience gained on the mechanical testing of rubber at the Gross-Lichterfelde Laboratory has been extended in so far that, in connection with certain points relating to the employment of ring test pieces for the tensile test, a large number of experiments were performed, which, in part, furnished interesting information. Moreover, attempts have been made to employ new apparatus for other tests in addition to the tensile test, and to collect experience therewith. These investigations have already been reported on elsewhere (see Memmler and Schob: "Mitteilungen aus dem königl. Materialprüfungsamte, 1911," Part IV, p. 186, and A. Martens: "Sitzungsberichte der königl. preussischen Akademie der Wissenchaften, 1911, Nr. XIV). Also at the Indiarubber Exhibition, held in London in 1911, the Laboratory made its labors known to wider circles by the exhibition of apparatus at its own stand, and by means of the paper read by myself. Unfortunately, the discussion at the London Indiarubber Congress failed to give the expected stimulus to this question of the mechanical testing of rubber—as also on other points—and it therefore seemed advisable to lay the essence of the newly obtained results before the VI (New York) Congress of the International Association, for discussion.

Our previously acquired experience on the actual tensile test; that is to say, the tensile test accompanied by observation of the course of elongation, led in general to the conviction that the ring test piece is superior to the hitherto customary rod-shaped test piece for this purpose, although it is not yet possible to disarm all objections to the ring test by means of experimental experience. In the absence of anything better, it was necessary to go more thoroughly into the peculiarities of the ring test, so that, in the event of the probable general application, the necessary experience would be already available. This was done. In the first place, it was of interest—for several reasons—to ascertain whether the method used in the Schopper-Dalen machine employed in the Laboratory, of causing the test ring to travel over the gripping rollers, exerts any noteworthy influence on the result of the test. Numerous experiments conducted in this connection have shown that the only way in which unimpeachable results can be obtained in tensile tests with annular test pieces of soft rubber is by causing the test piece to travel uninterruptedly over the rotatable gripping rollers throughout the experiment. The results obtained with a variety of materials differed very considerably in part, according as stationary or traveling rings were employed, the difference in one instance amounting to 75 per cent. Moreover, the influence varies very considerably in degree with the different kinds of rubber, so that the grading and valuation of the various kinds of rubber become unreliable when stationary rings are employed.

Another point to be investigated in connection with the general applicability of the ring test was the influence capable of being exerted on the results of the tensile tests by the method of making the rings, especially since objections have been raised, here and there, against the ring test that the method hitherto

*Paper presented at the 6th Congress of International Association for Testing Materials, New York, 1912.

employed for stamping out the rings in a stamping press was not impossibly attended with a preliminary straining of the material.

To afford an answer to this question, two different methods of making the rings were employed, namely, the method, already mentioned, of stamping out the rings in the Schopper press, and also cutting out the rings on a lathe. From each of the four kinds of rubber tested, 100 rings were made by the stamping process and 100 turned in the lathe. The results obtained show that, the influences exerted on the tensile strength by the stamping or cutting process are negligible, at least for tensile strength tests in practice. The fact that the different materials behaved differently in this respect indicates that a preliminary straining of the material so as to affect the tensile strength unfavorably is out of the question. In one material, stamping seems to have an adverse effect, while in another the cut samples gave the lower tensile values; and it therefore follows that neither method of preparation is unconditionally to be preferred, the selection of one or the other method for comparative tests depending on practical considerations. In any event, it is advisable, in making comparative tests with different materials, to employ the same method of preparation throughout.

It may be pointed out here that stamping the rings takes less time than cutting, and that, provided there is no variation in the thickness of the sheets, perfect uniformity in the dimensions of all the rings is insured by the stamping process. When the rings are cut, it is not always possible to prevent small variations in the dimensions, if only for the reason that the point of the cutter requires frequent setting, the cutter therefore having to be adjusted every time. On the other hand, the annular cutters used in stamping will last for 1,000 cuts or more, according to the material, before having to be resharpened, the operation, moreover, having no effect on the diameter of the rings. For reasons to be expounded later, it is desirable that a standard pattern should be established for the rings, for which purpose the stamping of the rings is to be preferred, as being cheaper, furnishing perfectly uniform rings from a given material, and producing rings quite as true to shape as those obtainable by cutting, provided the dimensions of the rings be properly selected.

A third, very important question, the solution of which presents special interest in connection with the establishment of a standard pattern for test pieces—namely, the influence of the dimensions (different widths and thickness[1]) on the results of tensile tests—has also formed the subject of extensive experiments at the Royal Laboratory for Testing Materials. The results appear to indicate that the influence of the dimensions of the test piece is confined to the breaking strength, and does not extend to the elongation at the point of rupture. This confirms results previously obtained by others (see Breuil: "Le Caoutchouc et la Guttapercha," 1904, No. 3, p. 56).

The only case in which the breaking strength is appreciably influenced by the dimensions of the rings is in that of material of high elongation, the tensile strength diminishing as the diameter increases, when the diameter is more than 0.1 cm. With a less ductile material this decrease, though perceptible, is far smaller; while with a still less ductile material such influence cannot be observed at all.

The fact that the more elastic kinds of rubber are more affected, in respect of tensile strength, by the dimensions of the test piece, whereas the elongation at rupture remains uninfluenced, seems to indicate that surface tension plays some part in the matter, materials with a high capacity for undergoing change of shape being more subject to such tension than others. In order to determine this influence it will be desirable to carry on further experiments in this direction. Probably also the abundant physical literature may afford valuable hints in this connection.[2])

Experiments have also been performed for determining the influence exerted by the internal diameter of the ring on the tensile and elongation values, the results, however, showing that no uniform relation can be detected.

Summarizing the experiences gained up to the present with regard to the tensile tests on soft rubber, it may be said that:

1. The test on rings is preferable to that with bars for several reasons;

2. Ring test pieces give unimpeachable results only when the test rings are allowed to travel over the tension rollers during the test;

3. The test rings can be prepared with ease and sufficient accuracy in a stamping press;

4. The determination of the elongation of soft rubber in tensile tests is not affected by the dimensions of the test ring;

5. For determining the breaking strength of soft rubber by means of tensile tests on rings, it is desirable to establish standard dimensions for the test pieces, since the tensile strength is influenced by the dimensions;

6. The objection to test rings—and equally so in the case of test bars—is that the rubber to be tested must be of such shape that the test rings can be stamped from it. It is therefore necessary to come to some agreement with regard to the manner of testing soft rubber mechanically in cases where the breaking test with annular test pieces cannot be applied.

Particular attention has been devoted to this last point in the recent work carried on at the Lichterfelde Laboratory for Testing Materials, the chief object of the experiments being to ascertain what

[1] "Thickness" denotes the height of the hollow cylinder.

[2] O. Frank; Annalen der Physik, Vol. 21, p. 602. — P. K. Bjerken: Wied. Ann. Vol. 43, p. 818. — W. C. Röntgen: Pogg. Ann., Vol. 159, p. 601. L. Schiller: Annalen der Physik, Vol. 22, p. 204.

method of testing soft rubber can be employed in place of the tensile test hitherto almost exclusively used.

The chief experiments were of the kind in which the material was caused to exhibit signs of wear in consequence of the application of continuous strain, the determination of such wear, by weighing the test pieces after a given length of exposure to the strain enabling a comparative estimate to be formed of the value of the different kinds of rubber. The experiments were carried out with different forms of apparatus, which have been frequently described in print[3]) and need not, therefore, be gone into any further at present. The Martens apparatus tests rubber balls 30 mm. in diameter, while the Mai apparatus on the other hand treats rubber rings like those used for tensile tests in the Schopper machine. The results obtained with the most divergent kinds of rubber in both apapratus indicate that the two methods are well adapted for practical use.

Whereas in these two methods the wear is determined in addition to the actual continuous strain produced by the application of pressure, an attempt has recently been made, at the Gross-Lichterfelde Laboratory, to elaborate a method specially applicable to kinds of rubber the practical uses of which primarily depend on their ability to stand wear, which method would also enable different qualities to be compared. This method will shortly be thoroughly described in the Mitteilungen aus dem königlichen Materialprüfungsamte. It consists in subjecting rubber discs (as a rule those formed in stamping out the rings for the tensile test) to wear by protracted rotary contact with emery in a receptacle, the progress of the wear being ascertained by weighing the test pieces.

In addition to these experiments which, as already mentioned, have furnished results and experience foreshadowing the practical utility of the methods, several new appliances, in accordance with the designs of Mr. A. Martens (the director), for the mechanical testing of rubber, have been set up in the Laboratory, and are at present in course of being tried. They are the following:

1. A press for simultaneously testing six rubber cylinders for susceptibility to changes of shape under pressure;

2. An apparatus in which ten rubber rings can be subjected to a definite preliminary strain by frequent repetitions of stretching and release, so as to enable the fatigue of the material to be determined by means of tensile tests applied before and after this strain.

3. A hardness tester on the principle of the Brinell ball test, for determining the hardness of specimens of rubber by the impression produced in the rubber disc by a small steel ball acting under a definite load applied for a definite time;

4. An apparatus for testing the platens of typewriters for resistance to continuous impact, by means of a small tup similar, in form and weight, to the type levers of a writing machine.

Finally, it may be mentioned that, in order to trace the progress of the changes of length in soft rubber test pieces under a stationary permanent load, a number of test bars of various mixtures of rubber are subjected to a continuous uniform load of 2 kilos per sq. cm. for a long period in a simple device. The progressive change in length is observed by means of lines marked on the test pieces, and the loading is continued until the length is found to remain constant several days in succession, the load being then removed and the contraction observed in the same way.

These test pieces have now been under observation in the Laboratory for about three years, and will continue so until rupture takes place in all of them.

In accordance with the proposals of Mr. A. Martens, similar continuous tests have also recently been applied to test rings, by stretching the rings over glass plates. In this way, the rings are subjected to a continuous stretch, determined by the width of the glass plate, and can be observed under different conditions of storage; for example dry, wet, warm, exposed to light, or exposed to the weather out of doors.

Reviewing the whole sphere of the mechanical testing of rubber as carried on at the Lichterfelde Laboratory, it will be admitted that the experiences gained in this field have been considerably widened since the last Congress at Copenhagen. That it is not yet possible to bring forward definite and perfectly elaborated proposals for generally applicable methods of mechanical testing for soft rubber is due to the peculiar physical and mechanical properties of this material and to its highly manifold technical uses. At the present time a committee of the German Association for Testing Materials is engaged on the points at issue, and it is hoped that further progress will have been made in this field by the date of the next International Congress.

Grain standards for Western Australia are stated to have been fixed this season at 62 pounds for wheat and 37 pounds for oats per bushel.

Oil-cake traffic in the world aggregates over 5 billion pounds yearly. Germany is the largest importer and the United States the heaviest exporter.

The world's sugar crop for the 1912-13 season is estimated at $18,052,216 tons, or 2,201,533 tons greater than last year.

[3]A. Martens: "Ueber die technische Prüfung des Kautschuks und der Ballonstoffe im königl. Materialprüfungsamte zu Gross-Lichterfelde (the technical testing of caoutchouc and balloon material at the Royal Laboratory for Testing Materials, Gross-Lichterfelde). Sitzungsberichte der kgl. preuss. Akad d. Wissensch, 1911, Nr. XIV. Memmler: "Mechanische Kautschukprüfungen und neuere Prüfeinrichtungen für diesen Zweck" (the mechanical testing of caoutchouc, and the new appliances for same), Kunststoffe, 1911.

REPORT ON THE ACTUAL STATE OF RUBBER ANALYSIS.*

By PROF. F. WILLY HINRICHSEN, Berlin.

In view of the great difficulties which the analyses of crude and of vulcanized rubber offer we should endeavor to agree upon the various methods of analysis, in order that similar tests conducted at different spots will lead to the same results. An international agreement upon this question would be particularly desirable.

I. ANALYSIS OF CRUDE RUBBER.

The crude rubber contains, as is well known, in addition to the caoutchouc proper and to the mechanical impurities, such as sand, bark, etc., also moisture, mineral constituents, resins and albuminoids. Of practical importance are above all the contents in pure rubber or caoutchouc, in mechanical admixtures, and in resins. The percentage of the latter affords a certain measure for the technical value of a kind of rubber, since the product is considered all the more valuable, the smaller its percentage in resins. The mechanical impurities are removed in the works by washing with water between rollers. The magnitude of the loss by washing is a second criterion for the aplicability and the value of a commercial product. This washing loss is ascertained in the laboratory in a similar manner as in the works, by washing a sample of rubber on a small experimental roller. It is primarily essential for these experiments that the sample selected represent a fair average of the product.

As regards the chemical analysis of crude rubber, we should in the first instance determine whether the test is to be made with the original material or with the washed material. It would in general appear advisable always to make use of the washed material which has been air-dried.

The moisture is suitably determined in a specially weighed portion by drying in vacuo over sulphuric acid at gentle heat, until the weight remain constnat.

For the determination of the resins 5 g. of the finely cut air-dried materials are completely extracted with acetone in a Soxhlet apparatus. Ten hours will in general be sufficient for this operation; the middle portion of the Soxhlet apparatus is suitably made of brown glass in order to prevent any action of the light on the material to be extracted. The dimensions of the apparatus to be used should be agreed upon, since any deviations from these dimensions would alone affect the values found for the percentages of the resins.

The further tests of the resins for optical activity and saponification which can be made according to Hinrichsen and Marcusson: permit under certain conditions to draw conclusions as to the botanical origin of the product.

Several processes have been suggested for the direct determination of pure caoutchouc; among these are the reaction with nitrous acid leading to the production of nitrosites, and the tetrabromide reaction. The recent scientific investigation of these two methods has led to the result that both these tests are unreliable. We are hence limited, as before, to an indirect analysis. For this we require, in addition to the already mentioned determination of moisture and to the extraction with acetone, in the first instance the estimation of the percentages of mineral constituents and of albuminoids. The former can as a rule be deduced from the determination of the ashes. An approximate measure for the proportion of albuminoids present is afforded by the determination of the nitrogen percentage which is suitably effected by the method of Kjeldahl. By multiplying the resulting figure by 6.25, corresponding to a content of from 15 to 18 per cent of nitrogen in the albuminoid, the amount of albuminaloids in the sample is approximately deduced. The difference between the component percentages of the impurities and 100 yields the percentage of pure caoutchouc in the material.

II. ANALYSIS OF VULCANIZED RUBBER.

The compositions of the various vulcanite rubber articles are so very manifold that a generally available method of analysis cannot be suggested. In many cases the constitution of the mixture cannot even approximately be ascertained by chemical means. When it is required to fix the conditions of supply for rubber materials, whose chemical composition is to be prescribed and to be controlled, we have for the present to bear the imperfection of our methods of rubber analysis in mind. Starting from this point of view the united German cable manufacturers have, for instance, prescribed for the standard leads a rubber mixture, which contains nothing but constituents that can be determined analytically with a certain degree of reliability, namely in addition to rubber and to sulphur only inorganic additions and hydrocarbons of the paraffin series (ceresin).

Since the methods for the direct determination of pure caoutchouc (nitrosite, bromide, etc.) are still less applicable to vulcanized products than they are to the raw material, we have to have recourse to the indirect analysis. In many cases the following mode of procedure will be satisfactory, especially when pitch, tar, asphalt, and similar materials are absent.

Five g. of the sample are extracted with acetone in the same way as we described above for crude rubber. This process will dissolve, in addition to the resins originally present in the rubber and to any foreign resins possibly added, the free sulphur, further oils, hydrocarbons of the paraffins, and wax. The sulphur is determined in a special sample in the residue, which remains after evaporating the acetone solution, after oxidation with strong nitric acid to which a little free bromine should be added. Solid hydrocarbons are approximately estimated by taking

*Paper presented at the 6th Congress of the International Association for Testing Materials, New York, 1912.

up the residue of the acetone solution with alcohol and by precipitating from this solution the hydrocarbons by continued cooling down to —5° C. When oils and foreign resins are present, an exact determination of the original rubber resin is not possible. The saponification figure does not constitute any measure for the amount of the additions, since some of the original rubber resins are themselves quite incapable of undergoing saponification, while parts of them may be highly saponifiable; it depends upon the origin of the material. When in addition to these resins only free sulphur and paraffin hydrocarbons are present, the resins may approximately be estimated by difference.

The material extracted with acetone is heated with hydrocarbons of high boiling point, for instance, petroleum or oil of paraffin, for the purpose of estimating the inorganic additions; these chemicals dissolve vulcanized rubber. The mineral additions (fillers) are, if possible, removed by filtration, if not, by centrifugation of the solutions which have been precipitated with benzine and have been washed with other organic solvents.

Another portion of the material which has been extracted with acetone, is boiled for four hours under application of a reflux condenser with semi-normal alcoholic soda lye. The lye will saponify the usual technical factices. After filtering off the unchanged material, water is added to the solution; by addition of mineral acids the facetice-acids are then precipitated, taken up with ether and determined. Any conclusion as to the percentage of the originally added factice is unsafe for this reason already, that the different kinds of commercial factices contain very strongly varying proportions of constituents soluble in acetone.

When we want to deduce the amount of pure caoutchouc in the mixture, we need now only proceed to the estimation of the bound sulphur. For this purpose we determine the total amount of sulphur in the mixture and we deduct from this the free sulphur, the sulphur which is inorganically bound, and the sulphur which is contained in the factice-acids.

The determination of the total sulphur is simplest and safest carried out by the other process, oxidation with nitric acid and with magnesium nitrate in a spherical flask, or by the Hinrichsen process, electrolytic oxidation in nitric acid. The sulphur which was bound by inorganic compounds is directly estimated in the filling materials, and the factice-sulphur is found in analysis of the factice-acids.

If we further know the moisture and the nitrogen (albuminoid) contents of the samples, the difference will give us approximately the percentage of pure caoutchouc.

When the mixture contains, in addition to the ingredients above specified, also tar, pitch, asphalt, or similar materials, any reliable analysis of the product may be regarded as out of question. Extraction by means of pyridin has formerly been proposed; it is inapplicable, however, since the pyridin also dissolves some rubber.

Prof. Gilchrist, of the Department of Agriculture of Armstrong College, has been making exhaustive experiments with soya bean cake as compared with decorticated cotton cake as a food for dairy cows. His published results show that the average qualities of these two cakes are very similar in chemical composition. The cotton cake is slightly richer in oil, while the soya cake is slightly the richer in flesh producers. The experiments show that, so far as these two cakes are concerned in feeding dairy cows, the one can be safely used as a substitute in a ration for the other. Although the results obtained were nearly equal for the two cakes, yet what slight advantage there was showed that soya cake was slightly better for milch cows than decorticated cotton cake. Some other points brought out by Prof. Gilchrist were: Soya cake being so highly nitrogenous in character, ought not to be used in larger quantity for dairy cows than about 6 pounds per head daily, and whenever used it should always be mixed with some other food particularly rich in carbohydrates or heat producers as distinct from foods rich in flesh producers. The nature of soya cake is not so well understood as that of decorticated cotton cake, and is consequently cheaper per ton, and on this account alone deserves favorable consideration at the hands of dairy farmers.

Most of the large German chemical firms have been able to maintain their previous rates of dividend during the past year. In some cases the dividends have been increased. Of the firms which do a large business in this country, either through agents or subsidiary limited companies, the following dividends are of interest:

Firms.	1911. Per Cent.	1912. Per Cent.
Aktiengesellschaft für Anilin-Fabrikation	20	20
Badische Anilin und Soda-Fabrik	25	25
Farbenfabriken Fr. Bayer & Co	25	25
Meister, Lucius & Brüning	27	30
Vereinigte Glanzstoff Fabriken	36	36
Aktiengesellschaft Schering	12	13
Chemische Fabrik von Heyden	12	14
Chemische Fabrik J. D. Riedel	12	12

The first four of the above-named firms do a large business in this country in aniline dyestuffs. The Vereinigte Glanzstoff Fabriken produce large quantities of artificial silk. The last three firms manufacture chiefly pharmaceutical products, and export largely to the United Kingdom and the colonies.

Salt is evaporated from ocean brine at Aden, Arabia, the production in 1912 being estimated at 105,000 tons. Probably 250 tons are consumed in Aden and 1,000 tons sent into the hinterland, while still larger quantities go to India as ballast for ships. It is generally understood that salt mines abound in the remote interior.

METALLURGY.

LABORATORY SINTERING.

BY H. B. PULSIFER.

The apparatus illustrated in Fig. 1 was assembled in the Metallurgical Laboratory of the Armour Institute of Technology for both experimental work and regular exercises in the metallurgical subjects.

Referring to Fig. 1 it will be seen that the roasting pot proper is situated between the motor and the suction fan, to which latter it is connected with a pipe. A working drawing of the cast iron roast pot is given in Fig. 2 and the same of the fan in Fig. 3. The motor is Western Electric Co. make, Type 180B; Volts, 110; Amp. 8.8; Rev., 1400; H. P., 1. The starting box is at the left in Fig. 1 while just behind the pot and between it and the fan is seen the gauge to indicate inches of water in suction as transmitted from the lower compartment of the pot. A liter bottle serves as reservoir for the liquid which is made conspicuous by the addition of a bit of aniline dye.

Fig. 1.

METHOD OF OPERATING.

The material to be roasted or sintered is preferably in a sandy or even finer condition: it is impossible to be too finely divided. Fine flue dust from iron blast furnaces, lead concentrates, copper concentrates, slimes or ores ground to pass 100 mesh all work equally well. Any dilutent or fuel which is to be added is also preferably reduced to a sandy condition. Lead or copper ores should have their sulphur reduced to some 12 to 16 per cent if it is not already as low; silicious or irony ores serve admirably. Iron blast furnace flue dust will probably contain too much carbon fuel and may be diluted with fine iron ore until from 8 to 10 per cent carbon is present; fine raw iron ores may have 8 to 10 per cent soft coal added as fuel.

The charge is first thoroughly mixed dry; water is then added until the material holds its shape well when squeezed in the hand; an extremely thorough incorporation is now given until the batch is apparently many times better mixed than necessary. The material will now be without lumps of any sort; it will pack together firmly if pressed or lay in a porous bed when carefully scooped into the roast pan.

The roast pan, itself, requires only to have its grate placed in position with all the holes free from any particles left from the former operation. Over the grate a layer of inert material is spread to protect the grate; this may be refractory material such as limestone, crushed crucibles, or iron ore, preferably about ¼ in. size and screened of anything which would pass the 3/16 holes in the grate. Sized material from a previous run is always suitable and thus introduces no foreign material.

The batch of well mixed ore is then carefully scooped into the upper and roasting section of the pot and the top is leveled off without pressing down the charge in the slightest degree; it is well to have the center of the surface a little depressed: the charge will likely sinter most quickly about the edges and if it is thinner in the middle it will then all finish at once. Besides this the air will draw through most easily about the edges and if the center is at all heaped up the ignition may be bad there and a soft spot left in the finished cake.

When the charge is placed and surfaced a layer of crumbled excelsior or sawdust is quickly spread over the surface, a match is applied to light the corners

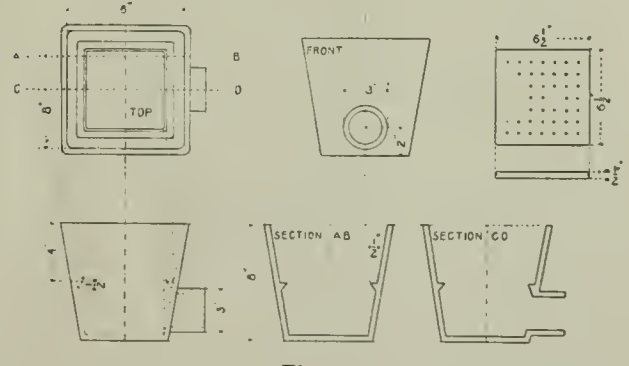

Fig. 2.

and center and the motor started. Ignition begins at once and spreads over the entire surface, any slow spots being helped by spreading on fresh burning kindling.

If conditions are right in the beginning ignition takes about a minute and the charge is then left to itself until the operation is completed.

The motor we use makes slightly over its 1400 revolutions per minute and the fan approximately 2,200 per minute; this commonly supplies a suction

of between 4 and 5 ins. of water as recorded on the gauge.

A charge should finish in from ½ to ¾ of an hour; two students can thus easily make a couple of runs during one laboratory period.

ROAST-SINTERING LEAD ORES.

Fig. 4 shows some cakes of roast-sintered lead concentrates. These concentrates came from the Daly-Judge mine at Park City, Utah. Such material contains about 30 per cent lead, 15 per cent zinc and nearly 30 per cent sulphur; when mixed with an equal weight of silicious Golden Reward gold ore from South Dakota the excellent cakes seen in the illustration can be made. The two top cakes in the center have been broken through the middle. Such sinter has been desulphurized to about 80 per cent; it is porous and firm, the ideal stock for blast furnaces.

The little roast pot will hold some 8 or 9 lbs. of a heavy lead mixture. The students have little difficulty

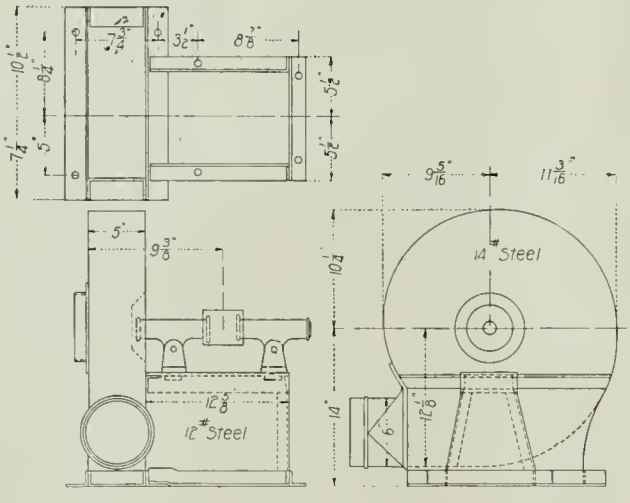

Fig. 3.

getting the moisture right but are greatly averse to sufficiently incorporating to fully avoid soft spots in the final cakes. The total amount of water may be exactly right but unless it, as well as each of the other components, is perfectly disseminated, soft and raw spots are liable to be found in the product.

To witness the soggy mixture ignite from the bit of kindling as well as to follow the remarkable progress of the fire zone down into the cake is an edifying experience for the students. The end of the run is taken as the time at which the rather thin pipe begins to cool noticeably.

As is well known, almost any mixture of lead ores which will supply even roughly the constituents of a lead furnace slag can be sintered if the sulphur and moisture is appropriate. Thus a great latitude is permissible in making up the charge; lead may be greatly in excess of that for a furnace charge, the mixture may be very high in iron or silica, lime might be high but for its bad effect in hindering desulphurization.

Lead ores make the most perfect sinter which one could desire. Besides the wide limits within which excellent results obtain the lead compounds fuse at low temperature and are naturally firm and tough. If the silica is a little coarse the lead compounds simply

Fig. 4.

fuse about such particles which keep their distance and prevent the whole mass from melting down into an impermeable fusion.

ROAST-SINTERING COPPER ORES.

Although there is no particular demand for such a process in present day treatment methods for copper

Fig. 5.

ores it is a valuable exercise for the students. The exercise illustrates the wide application of the process in general as well as the essential conditions—moisture and mixing—for each particular charge.

Copper ores give a sinter more granular and less tough and tenacious than lead ores do. The product

is, however, perfectly suitable for blast furnace work. Desulphurization is good and porosity possibly a little better than with leady material.

Fig. 5 is reproduced from a photograph of such a cake of copper sinter as broken through the middle. This cake was made from a mixture of equal parts of pure fine chalcopyrite and silicious gold ore. The result is quite similar to that produced by sintering a lead ore.

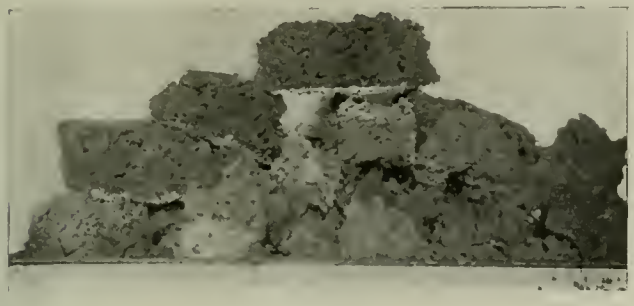

Fig. 6.

SINTERING IRON ORES AND FLUE DUST.

The experience of the author has been that the simple sintering of clean irony materials does not produce a cake fully up to the standard desirable for iron blast furnace work. It is not difficult to make a product beautifully granular and porous which will be too weak structurally. It is not difficult to make a product strong and tough but then it will likely be too massive and not at all granular.

Either fine raw ores or furnace flue dust sinters nicely with proper attention to moisture and mixing. In either case the carbon content should be some 8 to 10 per cent; raw ores will have this added in the form of fine soft coal and flue dust will be diluted with fine ore until the carbon content is right. A pulp which has been ground to pass 100 mesh sinters as well as the raw fine ore or sandy flue dust.

After much experimenting in the laboratory with the students during their regular exercises with the iron ore or flue dust it seemed not improbable that results of value might be obtained by annealing or by fritting the product usually obtained in the sintering pan. That it is not difficult to make fair cakes will be seen from Fig. 6, which is a photograph of a panful of cakes made in the usual way.

To improve on this material it was heated to various temperatures in a gas furnace and allowed to cool slowly; this made no observable change.

Further attempts to frit the material at still higher temperatures were eminently successful. At about 1150° to 1175° C. the granules begin to coalesce; the cakes should not be heated until they melt together but just to the fritting temperature. The porosity is little changed but a strength and toughness is assumed which now fits the material for the strenuous conditions in an iron blast furnace.

Fig. 7 shows such a piece from a cake first sintered in the pot on a layer of granular iron ore between it and the grate. The cake was removed from the pot and fritted in a gas furnace to 1175° C. Rather tender when removed from the pot, when slowly cooled from this temperature it is now firm and resonant.

This double treatment is of great significance, for, with a minimum of fuel the first granular cake can be produced under the very best conditions of ordinary sintering; then by merely passing the material through a furnace which may be operated continuously the cakes are gradually heated up to the fritting temperature and begin to coalesce throughout. This temperature is below that of the fusion point of the iron oxide and likely happens because of the ash of the coal first used or the impurities naturally present in the ore. In the illustration it will be noticed that while the cake proper is neatly fritted together the coarse lumps which served as a bed in the pan have scarcely been rounded at the corners.

With the double treatment, then, iron ores or flue dust can be made as suitable for the iron blast furnace as lead ores are suited to the lead blast furnace.

With constant speed for the fan it is interesting to note the intensity of the suction during the course of a run. After the first moment of ignition the suction

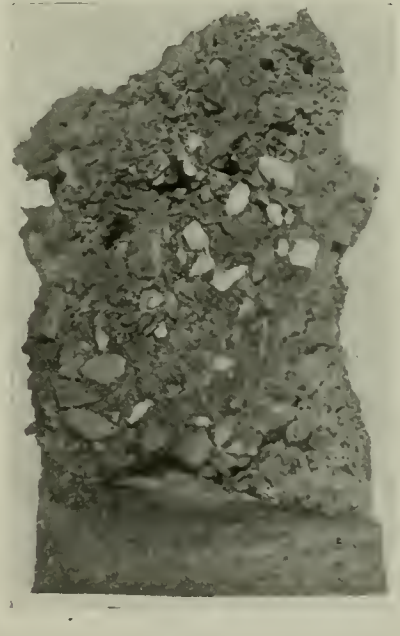

Fig. 7.

increases, during the portion of the run when the gases are most warm the suction is least, to again increase when the cake gets cold. The following indicated run was on a fine iron ore with 10 per cent ground coal:

Start	11:05	4.6 in. suction	30° exit gas
	11:07	4.9	35
	11:10	4.3	50
	11:15	3.5	75
	11:20	3.8	55
	11:25	3.8	40
	11:30	3.9	35
	11:35	3.9	33 cake finished

BISMUTH: ITS PROPERTIES AND THE SOURCES OF SUPPLY.

By T. H. OSBORNE.

Bismuth has been known for a very long period, even in the 15th century the name occurring; it was received from Basilino Valentino, and Agricola mentions it a century later. It has many qualities which render it useful in the arts and sciences. It is notable for its diamagnetic property, in consequence of which it is repelled by the poles of a strong magnet; thus a bar of bismuth, when balanced between the poles of a horseshoe electromagnet, places itself parallel to its arms, between the two poles, and not diagonally, as other metals. It is one of the poorest metallic heat conductors known, and is a silver white, lustrous metal, with a specific gravity of 9.83. It melts at 518° F. It occasionally may be mistaken for antimony, with which it has some resemblance, but its texture is more foliated. A remarkable property is that when cooling the metal expands about 2.3 per cent of its volume. This peculiarity has been taken advantage of in the production of alloys used in the production of stereotype plates. Another property is that it can be cooled 10° F. below its solidifying point and still maintain its liquid form; when at a given point solidification takes place, there is a simultaneous increase of temperature. Dry air has no effect on bismuth, but when exposed to moist conditions a reddish powder is produced over its whole surface. It burns with a bluish flame when it is raised to a red heat in air, and the yellow oxide Bi_2O_3 is formed. Its low thermal conductivity has already been mentioned; compared with silver, the proportion is 1.8 to 100. Bismuth is much used to form alloys, as the low melting point renders them extremely useful. These allows have melting points ranging from 140° to 201° F., the components being tin, cadmium and lead in varying proportions. One alloy made up of 50 per cent of bismuth, 25 of tin and 25 of lead, melts at 201° F.; also another, consisting of 20 per cent of bismuth, 30 of tin and 50 of lead. A useful alloy with the very low melting point of 140° F. consists of 50 per cent bismuth, 13 of tin, 10 of cadmium and 27 of lead; whilst one which melts at a temperature ranging from 150° F. to 158° F. is made up of 50 per cent bismuth, 14 of tin, 12 of cadmium and 24 of lead. By reducing the quantity of tin and substituting cadmium, the melting point is reduced. Bismuth can also be used for the production of an amalgam with mercury, with or without the addition of tin or lead, useful for some trade purposes. In very minute quantities the metal is used as a component of various anti-friction metals, only one-quarter per cent being used. For medicinal purposes bismuth has been found useful as the oxide, oxycarbonate, oxynitrate and salicylate. Another useful purpose is for a solder having the composition: bismuth 25 per cent, tin 50 and lead 25 per cent. It is extensively used for stereotypic plates combined with antimony 15 per cent, lead 70 and bismuth 15 per cent.

Bismuth is one of the few metals which the United States has to import, as not enough is produced to supply the whole of her own requirements. It is obtained in the States as a by-product in electrolytic lead refining. Large deposits have not been found in North America, but it is reported that in several mines producing gold and silver bismuth occurs in paying quantities. In several mines in Colorado and New Mexico considerable percentages of bismuth have been found, aggregating several tons. The average import into the United States is about 100 tons; the quanitity produced in the States does not vary from year to year. The main output comes from the works of the U. S. Metals & Refining Company, Grasselli, Ind. The lead ores treated there come from Utah. There are in addition some smaller producers of bismuth, but the total production is very limited, as during 1911 it only reached 33 tons. Bismuth has also been found in Montana and Nevada. The average annual imports in the States are 85 tons.

The world depends largely on South America for its main supply of bismuth. In Brazil ores of bismuth have been found in several localities, but the deposits have not as yet been developed, and it is not known whether they occur in paying quantities. Bolivia is the largest bismuth-producing country; exports during 1909 reached 215 tons, valued at $190,000, whilst the quantities for 1910 and 1911 were approximately the same. In Bolivia bismuth is generally found with other metals, but whilst elsewhere the separation is an intricate one, in Bolivia it is relatively simple. The main output is from the Tazna district, but it occurs generally in the noted mineral zone extending from Huayna to Potosi, the main centers being La Paz and Chorolque. The price obtained for the Bolivian bismuth is a very steady one, and does not vary from year to year. The crude bismuth exported from Bolivia and Peru contains the following metals:

	Bolivia.	Peru.
Bismuth	99.04	93.56
Copper	0.27	2.07
Silver	0.08	.....
Antimony	0.56	4.57

In Chile bismuth occurs as an alloy with silver, which is named Chilenite, and is found near Potrero Grande, in the San Antonio mines.

BISMUTH IN AUSTRALASIA.

Bismuth is also found in Queensland, Australia, about 25 miles from the town of Herberton; the mines are situated some 150 miles from the sea. Within a few miles are the Glenlinedale tin mines; silver and copper are also found in the vicinity. These bismuth mines were first opened out about seven years ago, but the mineral which then attracted attention was wolfram, at that time commanding a high price. The bismuth, which occurred as a carbonate, was overlooked, and ultimately the workings were abandoned. More

recently the mines were reopened and the bismuth ores received greater attention, a market was found and concentrates sold at remunerative prices. The prevailing rock of the country around is biotite granite, in which the veins of ore occur; they are horizontal, and at present three or four are known. It is possible that there are others at a lower depth, but until shafts have been sunk that must remain a supposition. Those now known outcrop on rising ground, and there may be others at a still higher level; but until the district has been more thoroughly surveyed the exact relationship and number of veins cannot be described. The veins vary in thickness from 8 to 13 ins. They are made up of topaz, the carbonate of bismuth and wolfram. They have been located by shallow sinkings over an area about half a mile in extent without their limits having been reached. After the vein matter has been mined, it is carefully hand-picked, and the ore when sent to the crusher contains 7 to 8 per cent of bismuth; it is then jigged repeatedly and a concentrate is obtained, which is readily sold. There is some loss through the carbonate sliming, which more perfect appliances and system may save. In Victoria near the town of Maldon, bismuth is found as a natural alloy with gold, the mineral being called Maldonite, the composition being Au_2 Bi. The crude bismuth produced in Australia contains the following ingredients:

Bismuth	96.2
Antimony	0.8
Copper	0.5
Lead	2.1
Iron	0.4

Small quantities of bismuth are also obtained in Tasmania; the output for 1909 was 3½ tons, valued at about $6,000, and during 1910 the quantity reached 10¾ tons, the value being $20,500.

BISMUTH IN EUROPE.

In Saxony bismuth is derived from lead and silver ores, it is found there as an oxide, together with litharge. Up to the year 1872, the world's total yearly output only reached 25 tons, of which about 18 tons came from Saxony, the yield of mines near Schneeberg. Bismuth ores have also been obtained from mines in the Joachimsthal, Bohemia. Bismuth-silver-lead ores likewise occur in Saxony and are smelted at Freiberg in that country; there are other smelteries at Altenberg. The bismuth market is largely controlled by the Saxon Government and an English company, who to a large extent have a monopoly of the trade; they control the sources of supply and are able to maintain prices at a remunerative level. A bismuth ore occurs in Saxony not known elsewhere, named Pucherite, it is a bismuth vanadate of a reddish-brown color. The refined bismuth produced in Saxony contains 99.98 per cent of the metal; with .03 of copper and 0.06 of lead; a less pure output contains 99.74 of bismuth with minute quantities of arsenic, copper, lead, sulphur and silver; the aggregate of these impurities being 0.25 per cent only. In South Germany a bismuthenite combined with chalcocite has been found, and is known as Wittichenite, after the town near which the mine occurs.

In Germany the smelting process consisted of a roasting of the ore, resulting in a uranium-bearing slag, a cobalt speiss and crude bismuth matte, from which the bismuth may be obtained by crystallization. In some smelteries after oxidation the ores were subjected to a hydrochloric-acid bath, from which the oxychloride of bismuth is precipitated in water. Coke carbon is added to the dry oxy-chloride, with sodium carbonate and glass. Iron crucibles are used for the smelting and the bismuth is offered for sale in bars. In France the oxidized ore is treated in hot hydrochloric acid, the bismuth being precipiated by iron from the solution. The smelting is effected under a layer of carbon.

REFINING.

Before crude bismuth such as that produced in Australia, Bolivia or Peru is available for industrial purposes, it has to undergo a refining process. For this purpose advantage is taken of the slight affinity, which the metal has for oxygen and a process has been devised akin to that employed for refining lead. The bismuth is raised to melting point and while in the fluid state is exposed for a suitable period to the air, with its contained oxygen. Impurities such as antimony, arsenic, iron, sulphur, tin and zinc are eliminated, generally by volatization and refined bismuth obtained, with occasionally only .02 per cent of impurities.

The preliminary processes to which the concentrated ore has to pass through are roasting and smelting. Some of the ores are first crushed to pass through a sieve with four meshes to the lineal inch and are there roasted with carbon. For this purpose long hearth reverbatory furnaces are recommended, in preference to heap and kiln roasting, which do not give satisfactory results. A reverberatory furnace with a hearth 16 feet by 9 feet has been found ample for nearly seven tons of ore daily. The ore during the process must not be allowed to agglomerate, otherwise any contained arsenic or antimony would not volatilize. For smelting a reverbatory furnace may be used, crucibles are also employed.

BISMUTH MINERALS.

Bismuth rarely is found as an oxide; many ores are known, but the degree of purity is not generally sufficient to enable mines to be worked for that metal alone. Among the minerals the following may be mentioned: bismuthinite, bismite, bismutite, bismutospharite, uranospharite, pucherite, guanajuatite. Double sulphides occur with copper, lead and silver. Native bismuth is a heavy mineral, approaching black in color with a tinge of gray, when first exposed there is a pronounced metallic luster, inclined to pink. It often occurs in granular masses, both brittle and

sectile in character. The average specific gravity is 9.7. Various elements occur with it occasionally in minute quantities, such as arsenic and sulphur, tellurium has also been found. The bismuth ores generally contain 10 to 20 per cent of the metal; they may sometimes be found in the quartz and pegmatite veins intersecting gneisses, granites and slates. The bismuth ores often contain noticeable quantities of iron and copper pyrites, sulphides of cobalt and nickel, galena, zinc blende, barytes and hematite, as well as minerals of gold, silver and antimony. The bismuth sulphide Bi_2S_3, known as Bismuthinite has a specific gravity of 6.5; it is a brittle mineral of a color approximating to lead, and crystallizes in the orthorhombic system; it is both fusible and sectile. The proportion of bismuth averages 80 per cent. Bismulite is a hydrated bismuth carbonate ranging from white to yellow in color, with frequently as much as 90 per cent of metal; its specific gravity ranges from 7 to 7.5.

ABRASION TESTS OF STEEL.*

By FELIX ROBIN, Paris.

In compliance with a request which has been addressed to us we beg to offer a résumé of the conclusions drawn from experiments, which we conducted in 1909 and which were published by the Iron and Steel Institute (Carnegie Researches 1010[1]). The abrasion of which we speak is quite of a special kind. It consists in the wear of steel when rubbed under a certain pressure on papers which are covered with some abrasive powder. The abrasion number is the sum of the weights of metal lost by abrasion by three consecutive tests, each lasting a minute. The steel specimen is cylindrical, 50 mm in diameter; the normal experiments are conducted with a run of 200 m, the circular path described by the specimen having a diameter of 150 mm, the pressure being 1 kg per sq. cm., and the speed 70 revolutions per min.

For the same type of steel and for the same abrasive, two sheets of different papers give well-comparable results. The precision of the tests attains from two to four per cent with Oakey paper; with Denis Poulot and similar papers it is 10 per cent for ordinary steels, and 20 to 15 per cent for tempered very hard steels.

The general observations which we have made are the following:

Pressure.—Pressure augments the wear approximately proportionately if within 0.5 and 2 kg. per cm^2. In hard steels the wear increases at a more rapid rate, and the curve is parabolic. The wear is proportional to the surface of the specimen.

Speed.—The speed of the apparatus increases the abrasive power of the paper. Some steels are more sensitive in this respect than others; such as especially those which are also sensitive to variations in the pressure.

Nature of the Abrasive.—Different abrasive materials and papers of different sizes of grain class the metals in approximately the same order, while they give different figures as functions of the abrasive power.

Wear of Steels.—In the case of annealed carbon steels the wear is not proportionate to the contents in pearlite. We find a maximum of abrasion with 0.4 per cent of carbon; in hypereutectoids the wear is approximately proportional to the carbon percentage.

Increased Fineness of the Particles, Cold Work, the Presence of Phosphorus Increase the Resistance to Abrasion, the Presence of Silicon and Manganese Diminish it Frequently.—In cast metal the resistance grows with the phosphorus contents and with the percentage of iron carbide. The hardened steels can badly be distinguished by this process; on the contrary tempered steels lend themselves to this examination without any difficulty. The best resistance in hardened steels seems to be characteristic of the finest martensites.

Special Steels.—Chromium increases the resistance of annealed steels noticeably, it has little effect on hardened steels. Double carbides have a very great resistance. Austenitic steels or steel containing nickel or manganese offer a remarkable resistance to abrasion; we find in these frequently the opposite effects as those brought out by the Brinell tests. The comparison between the different methods of procedure for measuring the hardness and the measurement of the abrasion leads us to offer some remarks which will be of interest. In certain cases of great hardness the wear will give results when the ball hardness tests does not any longer show any sensitiveness; the indications of the two methods may be of the same sense or of opposite sense; according to the products experimented upon.

These results might be attributed to multiple causes, and among them intervene in the first instance the mineralogical hardness and the brittleness.

The practical conclusions to be drawn for the domain of the science of testing are the following: each mode of measurement and each kind of test leads to a special classification of the steels. The diverse modes of determining the wear can not be estimated by one and the same test. The test which we just explained so far only appears to lend itself for the examination of rails under certain, special service conditions, to files, and to apparatus for disintegration, etc.

[1]Compare also "Revue de Métallurgie," 1911.

*Paper presented at the 6th Congress of the International Association for Testing Materials, New York, 1912.

The Ontario salt industry, which comprises practically all the Canadian production, is confined to the southwestern peninsula, covered by the Windsor and Sarnia consular districts. The 1912 yield was 88,689 tons, valued at $430,835. The industry employed 216 workmen, who received in wages $121,477.

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NOTES AND COMMENTS.

Binders for Fuel Briquets.

Experience in European countries and investigations made at the fuel-testing plant of the United States Geological Survey at St. Louis, and later by the Bureau of Mines at Pittsburgh, have shown that lignite may be successfully briquetted without the use of any additional binding material, and that the most satisfactory binders for anthracite, semi-anthracite, bituminous and sub-bituminous coals are coal-tar pitch, gas-tar pitch and asphaltic pitch, or inexpensive cementing mixtures that are practically waterproof. Of the 19 briquetting plants in commercial operation in the United States during 1912, 10, according to E. W. Parker of the United States Geological Survey, used as a binder coal-tar pitch, or mixtures in which it is the chief ingredient; 1 plant used asphaltic pitch, 2 used water-gas pitch, 4 used mixed binders whose composition is not made public and 2 (1 operating on peat and the other on carbon residue) used no binder. The number of plants using coal-tar pitch as a binder exceeded all the others put together. Inorganic binders, such as cement, have not given satisfactory results, for although they may form efficient cements, they have the serious objection of increasing the ash and adding nothing to the combustible elements of the fuel. Binders made of organic material, however, such as pitches from coal-tar, gas-tar or asphalt contribute combustible material and do not increase the amount of ash.

Condenser Tubes.

A number of interesting papers have been presented before the British Institute of Metals, among which should be particularly mentioned "The Corrosion of Brass Condenser Tubes" by Mr. Paul T. Bruhl. This paper is the result of a thorough study of this troublesome problem and brings out certain very interesting conclusions arrived at by the author. "In this connection attention should be called," says Carl F. Woods of the staff of Arthur D. Little, Inc., chemists and engineers of Boston, "to the proceedings and the report of the corrosion committee of the institute which was opened a year ago with a view to carrying out an exhaustive and authentic research on the corrosion of brass and bronze. The committee have decided to erect in Liverpool a plant in which the conditions of marine condenser service should be as closely imitated as possible. The plant is to consist essentially of four cast iron tubes each fitted with tube plates to carry 12 condenser tubes, these iron tubes representing four small independent condensers. The condensers will be connected direct to the exhaust of a small engine which in turn will drive a circulating and vacuum pump for circulating sea water through the condensers. Each condenser will be fitted with the same kind of tubes and the committee has decided for the first set that one condenser shall be equipped with the so-called 'Admirality' mixture with a tube plate of naval brass, the equipment being carried out with the same extreme care insisted upon by the 'Admiralty' practice. The second condenser will represent the best class of commercial practice, the tubes being 70-30 mixture and the plates of yellow metal. The exact equipment of the other two condensers had not been decided upon at the time of the committee's progress report, but they will be compositions representative of commercial practice. The results obtained from careful experiments carried out in this way should be of the utmost value, as it should be possible to practically duplicate service conditions and at the same time to control the various conflicting conditions in such a way as to arrive at definite well-founded conclusions."

Voltite.

A particularly interesting invention is that of "Voltite" by Mr. Arthur T. Firth of New Zealand, which in brief is a method for the electro-plating of one metal on another by frictional precipitation. "The electro-plating of metals has grown rapidly to an in-

dustry of great importance," says Mr. Carl F. Woods, secretary to Arthur D. Little, Inc., "but up to the present time there has been a great deal of economic waste owing to the practical difficulties in the way of replacing the electro-deposited metal which is lost by the friction of constant use. A number of attempts have been made to solve this problem and several patents have been issued, but in most instances the coating possible of application to the metal by this process is so thin as to be of little value.

A recent patent was issued for the deposition of nickel and other metals by friction which created considerable discussion in the electro-metallurgical world, but after a series of careful experiments it was found that the energy used in the process was so great in proportion to the results that the process possessed more theoretical than practical value.

The process invented by Mr. Firth is electrolytic like other electro-plating operations but very much simplified, and it is claimed for the invention that anyone of ordinary intelligence can operate the process successfully. The compound itself, water and the slight friction used in applying it, form a voltaic action, the metallic powder forming the anode and the article on which it is to be deposited the cathode; hydrogen is developed which reduces the salt to a metallic state upon the article itself. The operation is applicable to gold, silver, nickel, copper, tin and brass, and one of the most interesting applications is that of silver direct to steel. Perhaps the biggest field for its application lies in household use. The constant cleaning of silverware results in the removal of the deposited metal, whereas the use of "Voltite" is claimed to increase the thickness of the metal instead of decreasing it and at the same time to preserve the desired appearance of the article."

Three New Alloys.

In their last official report as chemists to the American Institute of Metals, Arthur D. Little, Inc., of Boston, mention three new alloys among the various items of recent progress in the metal industry.

A French patent has recently been issued covering the production of two types of alloys from copper, zinc and silicon, which are claimed to possess great tenacity, resistance to acids and alkalies and to be capable of rolling into finished shapes.

Another new alloy has been patented by the Ajax Metal Company composed of iron, nickel and copper, which is claimed to be non-corrosive, malleable, of great tensile strength and capable of being rolled, drawn or cast.

A new type of pyrophoric alloy has been patented in Germany which consists of the addition of 5 per cent metallic cerium to an alloy of manganese and antimony. The inventor claims excellent pyrophoric properties from this alloy which is essentially different from the other alloys of this type in which cerium is the main source of the pyrophoric characteristics.

RECENT PATENTS.

The following patents relating to industrial and engineering chemistry are reported by C. L. Parker, solicitor of chemical patents, McGill Building, Washington, D. C.:

1,051,876. Process of Obtaining *By-Products* from the Gaseous Distillation of Fuels. William Feicks, Bloomfield, N. J. Patented February 4, 1913.

1,051,882. Process of Treating *Waste Gas-Purifying Material.* Henri Gouthiere and Pierre Ducanel, Rheims, France. Patented February 4, 1913.

1,051,926. Solidified *Hydrogen Peroxid* and Process of Forming Same. Fritz E. Stockelbach, Detroit, Mich., assignor to Frederick Stearns & Co., Detroit, Mich., Patented February 4, 1913.

1,051,978. *Varnish and Paint* Remover. John W. Alexander, Parkersburg W. Va., assignor of one-half to Percy C. Parker, Parkersburg, W. Va. Patented February 4, 1913.

1,052,098. Method for Determining the Content of *Butter Fat in Butter.* Roscoe H. Shaw, Washington, D. C. Patented February 4, 1913.

1,052,113. Process for Refining *Sugar.* Hermann Wiese, Wallaceburg, Ont., Canada. Patented February 4, 1913.

1,052,145. *Pigment.* Robert Hochstetter, Cincinnati, Ohio. Patented February 4, 1913.

1,052,469. Process of Making *Edible Oils.* Carleton Ellis, Montclair, New Jersey. Patented February 11, 1913.

1,052,693. *Aluminum-Solder.* Richard Seifert, Union Hill, New Jersey. Patented February 11, 1913.

1,052,727. Process of Extracting *Aluminum* from Its Ores. Alan Kissock, Golden, Colorado. Patented February 11, 1913.

The process consists in forming an intimate mixture of aluminum bearing material, sufficient carbon to convert the contained aluminum into aluminum carbid, and the required amount of some suitable compound of sulfur to change the aluminum carbid into aluminum sulfid, and heating the same to a viscous condition, and extracting aluminum.

1,052,797. Process of Manufacturing *Sulfate of Ammonia.* Emil Collett, Christiania, Norway. Patented February 11, 1913.

1,052,815. Process of Making *Nitrogenous Compounds.* Charles J. Greenstreet, Indianapolis, Indiana. Patented February 11, 1913.

The process which consists in passing nitrogen over calcium hydrid and carbon heated to a temperature above a dark red heat.

1,052,853. Separation of *Tar and Ammonium Chlorid* Contained in Gases Produced by Distilling Coal. Louis Solvay, Brussels, Belgium. Patented February 11, 1913.

1,052,924. Process for Manufacture of a Product from Which *Red Lead* Can Be Burnt. Georg Jan-

sen, Dusseldorf, Germany. Patented February 11, 1913.

1,053,074. Process of Generating High-Pressure *Oil-Gas*. Rudolph Vuilleumier, New Rochelle, N. Y. Patented February 11, 1913.

1,053,349. Art of Removing *Tar* from Coal-Gases. William H. Blauvelt and Charles G. Tufts, and Clarkson A. Collins, New York, N. Y., assignors to Semet-Solvay Company, Solvay, N. Y. Patented February 18, 1913.

1,053,436. Process for Reduction of *Ores*. George F. Rendall, New York, N. Y., assignor to R. W. Priest, trustee, New York, N. Y. Patented February 18, 1913.

1,053,454. Process of Improving the Quality of *Malleable Iron and Steel*. Otto Thallner, Remscheid, Germany, assignor to Elektrostahl G. M. B. H. Remscheid-Hasten, Germany. Patented February 18, 1913.

1,053,456. Production of *Ammonium Nitrate* from Ammoniacal Gases. Friedrich Uhde, Gerthe, Germany. Patented February 18, 1913.

1,053,486. Process of Treating *Ores* Preparatory to Magnetic Separation. James B. Etherington, Winthrop, Mass., assignor to Campbell Magnetic Separating Company, a Corporation of Arizona. Patented February 18, 1913.

This is a process of treating ore, containing non-magnetic iron sulfids, consisting of subjecting the same to heat in a non-reducing atmosphere until the iron sulfids become magnetic, and then removing the same from the action of heat before the iron sulfids are converted into oxids.

1,053,592. Process for Condensing *Metallic Vapors*. Frederick W. Gordon, Fort Washington, Pa. Patented February 18, 1913.

1,053,624. Process for the Reduction of *Stannic Oxid*. Zdenko Metzl, Rouen, France. Patented February 18, 1913.

1,053,652. Manufacture of *Varnish*. Herbert Schuleter and Charles Zimmerman, Jr., New York, N. Y., assignors to New Process Varnish Company, New York, N. Y., a Corporation. Patented February 18, 1913.

1,053,761. Process of Treating Commercial *Calcium Cyanamid*. Frank S. Washburn, Nashville, Tenn. Patented February 18, 1913.

1,053,798. *Tanning Composition* and Process of Making the Same. Amos G. Ernst, Junction City, Kans. Patented February 18, 1913.

1,054,051. Preparing *Coke* for Charging Blast Furnaces. Marcus C. Steese, Youngstown, Ohio, assignor of one-half to Rollin C. Steese, Youngstown, Ohio. Patented February 25, 1913.

1,054,247. Manufacture of *Dyes* of the Cerulein Series. Arnold Steiner, Basel, Switzerland. Patented February 25, 1913.

1,054,250. Process of Obtaining Pure *Phosphorus Sequisulfid*. Alfred Stock, Breslau, Germany, assignor to Chemische Fabrik Griesheim Elektron, Frankfort-on-the-Main, Germany, a Corporation of Germany. Patented February 25, 1913.

1,054,324. Process for Producing *Diastatic Product*. Jokichi Takamine, New York, N. Y. Patented February 25, 1913.

The process consists in sowing diastatic spores upon a culture medium and subjecting the same to incubating conditions while securing air contact by keeping the mass normally in agitation.

1,054,373. Method of *Silicidizing* Articles Containing Carbon. Frank J. Tone, Niagara Falls, N. Y., assignor to The Carborundum Company, Niagara Falls, N. Y., a Corporation of Pennsylvania. Patented February 25, 1913.

1,054,400. Method of Making *Ferric Chlorid*. Herbert H. Dow, and Arthur E. Schaefer, Midland, Mich., assignors to The Dow Chemical Company, Midland, Mich., a Corporation of Michigan. Patented February 25, 1913.

1,054,414. Treating *Sugar Liquors*. Faustin Hlavati, Berlin, Germany. Patented February 25, 1913.

1,054,515. *Explosive Compound*. Charles F. Dippel, Brenham, Tex., assignor of one-half to Dilmus E. Teague and Ernst G. Langhammer, Brenham, Texas. Patented February 25, 1913.

1,054,518. Process of Making *Potassium Sulfate*, etc. Charles A. Doremus, New York, N. Y., assignor of one-half to John S. Hoyt, Darien, Conn. Patented February 25, 1913.

A continuous kiln for the firing of pottery, which is now working successfully at the factory of the Empire Porcelain Co. of England, is described as follows in a recent issue of the Staffordshire, England *Sentinel:* The kiln in which the ware is fired is a circular tunnel, having a continuous slot in the roof, through which hang 28 suspension bars, each bar carrying an iron basket, in which the ware is placed. The slot is covered over with a suitable cover, the lower edges of which are sealed by being immersed in sand grooves, and loss of heat is thereby prevented. The 28 suspension bars, carrying the iron baskets in which the ware is placed pass upward through the slot in the roof of the tunnel, and are attached to an iron superstructure, which stands above the kiln. This superstructure is built upon and carried by a central pillar, which revolves upon ball bearings. The whole weight of the superstructure, ware and baskets being thus carried upon ball bearings, the driving power required to revolve the whole load is thereby reduced to minimum when fully working. The baskets of ware upon one side of the kiln balance the baskets of ware upon the other side. There is only one firing mouth, and this is placed upon one side of the kiln, and upon the opposite side is the charging door for placing in and removing the baskets of ware.

The municipality of Havre, France, has granted a franchise to Les Frigorifiques de l'Alimentation Havraise, composed of local capitalists, for establishing a cold storage plant at the municipal abattoirs. The contract—approved by the municiapl council on March 14, 1913—makes the proposed plant a quasi-official enterprise. In fact, it is treated as a public utility. The company's operations will comprise two distinct branches—the abattoir plant, for which it will receive 10,764 sq. ft. in the abattoir enclosure, and the commercial or public plant, which may receive all kinds of food products in storage and manufacture certain by-products. For the latter the municipality will sell to the company 43,055 sq. ft. at $4.825 per square meter (10.764 sq. ft.). The product of the sale, $19,300, will be devoted by the city to needed improvements in the slaughterhouse itself.

Germany's foreign trade in chemical products during the five years ending Dec. 31, 1912, showed an increase during the period of 38 per cent in exports and 26 per cent in imports. The values of exports and imports for the two years including this period were as follows: 1907, exports, $142,053,000; imports, $72,685,200; 1912, exports, $195,486,000; imports, $91,670,000. Raw materials form the larger item of import in this branch. Thus, leading all others in 1912 was Chile nitrate of soda, aggregating 813,000 metric tons, of a value of $35,793,000, as against $32,182,000 worth of this product in 1911.

The Manchester (England) *Guardian* reports that a mixture of gasoline and paraffin has been submitted to tests by the British Motor Cab Co. and been found most satisfactory. The cost works out at 21 cts. per gallon, and the fuel has been made practicable for car-running purposes by means of a starting device which the company has just patented. The general manager says that the company now has 1,250 cabs running on the mixture, and with the starting device, and that better mileage is obtained than with petrol or gasoline.

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STERILIZATION OF WATER BY ULTRA VIOLET LIGHT.*

By JOHN R. DAVIES.

It has been known for a long time that sunlight possesses marked sterilizing power; also that sunlight contains ultra violet light. No connection was made between these two facts, however, until comparatively recent years. In 1887, Davis and Blunt did the first work on the bactericidal action of ultra violet light.[1] Since then many men have worked on the problem, and the results of their work seem to be conclusive that the ultra violet ray possesses a bactericidal action to a high degree.

Courmont and Nogier, in 1908, proved that the sterilizatin of polluted water, by means of ultra violet light, was complete at the end of 1 to 2 minutes.[2] They also found that the sterilizing action was direct, and not due to the formation of H_2O_2 and O_3 in the water.[3] At this time these men stated that the active rays were those less than 3,000 Angstrom units in length, but a few years later Mme. de Cornovodeau and V. Heinri showed them to be less than 2,200 Angstrom units in length, and that rays longer were useless for purposes of sterilization.[4] That the ordinary turbidity of water and the presence of colloids prevent to a high degree its sterilization by this method was shown by Henri, Helbronner and Recklinghausen in 1910.[5] In the same year, Vollet showed that clarification of the water resulted in more rapid sterilization.[6] Biijuvid, in his work, was able to show that the heating effect of the light did not bring about sterilization, for the temperature of the water rose only from 0.2 to 0.3° C. in the time required.[7] Gaiter observed that the bacteria, after exposure, became coagulated and granular in appearance.[8] Cornovodeau and Henri did a great deal of work on the resistance of different bacteria toward the light from a quartz mercury vapor lamp; with the lamp at a distance of 5 cm. from the surface of the water the bacteria were destroyed in the following time:

B tetanus	20-60 seconds
B coli	10-20 seconds
B typhosus	15-20 seconds

Courmont, Nogier and Rochaix in 1909[9] found that B coli, for a radius of 30 cm. around an immersed lamp, were destroyed in 1 minute.[10]

The question as to the sterilizing action of the light, whether direct or due to the formation of H_2O_2 or O_3 in the water seems to have been conclusively settled by several workers. Kermbaum, in 1909, even went so far as to question the presence of O_3 or H_2O_2 in water after 10-14 hours' exposure. Cenovadeau and Henri, in the same year, found that after 30 minutes' exposure there was formed 1/5 of 1 mg. of H_2O_2 per liter; later they found merely traces of either H_2O_2 and O_3 after 20 minutes' exposure. In the time required to sterilize water containing 1,800 B-coli per cc., Courmont, Nogier and Rochaix could not find a trace of H_2O_2 or O_3 in the water.[11] Reschel, in 1908, discovered that 1.5 gs. H_2O_2 per liter of water was a sufficient dose to destroy typhoid bacilli after 6 hours' contact. He also proved that water sterilized by ultra violet light rays in a few seconds was not sterilized by 1.19 gs. of H_2O_2 per liter after contact of over 3 hrs.[11] This amount of H_2O_2 is 6,000 times as strong as that found by Cernovodeau and Henri after 30 minutes' exposure.[11] This I believe is conclusive evidence that the sterilizing action of the ultra violet ray is direct.

In the light from an arc lamp there is present a great deal of ultra violet light, but when iron arcs are substituted for the carbons, the intensity of the ultra violet light is greatly increased. Knowing the sterilizing properties of the ultra violet rays, the problem which was suggested was this: Is there sufficient ultra violet light present in the light produced from the iron arcs in air to sterilize water in a manner similar to that from the mercury vapor lamp?

Of the many phases of this problem, only the following were attacked:

*Paper presented before the Illinois Water Supply Association.

†Assistant in Chemistry, Northwestern University, Evanston, Illinois.

[1] Compt. rend., 149, 810.
[2] Compt. rend., 148, 523.
[3] Compt. rend., 149, 364.
[4] Compt. rend., 150, 52.
[5] Compt. rend., 151, 677.
[6] Compt. rend., 150, 1076.
[7] J. Gasbel, 54, 853.
[8] J. Gasbel, 54, 853.
[9] Compt. Rend., 150, 52.
[10] Compt. Rend., 149, 150.
[11] Compt. Rend., 150, 1453.

I. Relation of time to distance.
II. Penetrating power.
  a. In relation to depth of the water.
  b. In relation to turbidity.
  c. In relation to interposed substance.

The lamp used in the experiment was an ordinary stereopticon lamp with the carbon arcs replaced by iron rods one centimeter in diameter; these wore down about 0.05 centimeters in length per hour, during the passage of the current. The lamp, in circuit with an ammeter and a rheostat, was connected with a direct current generator, 110 volts and 6 amperes. A polished tin reflected or concentrated the rays of light upon the exposed surface. The iron oxide, which was formed, instead of dropping into the water beneath, rose in a cloud and deposited upon the reflector above. The length of the spark was 0.75 centimeters.

The water was collected in a large receiver containing polluted organic matter, and was allowed to stand at room temperature for several days to insure the presence of a large number of bacteria. No attempt was made to identify the bacteria present during the experiment. Control tests showed the presence of 15,000 to 20,000 bacilli per cubic centimeter. In the tables showing the results of the experiment there is listed only the minimum time required for the sterilization of the water at each respective distance. Each experiment—for instance, to find the time required to sterilize water 1 cm. in depth, at a distance of 5 cm. from the lamp—required 20 to 30 observations, all of which were duplicated before any conclusions were drawn. The water was exposed in crystallizing dishes.

(a) On the relation of the distance from the source of light to the exposed surface to the time required for sterilization.

The water which showed the presence of 20,000 bacilli per cc. was placed in the container to a depth of 2.5 cm. The lamp was adjusted so that the arc would be at the required distance from the surface of the water. The final results are as follows:

Distance, in centimeters.	Time, in seconds.
5	20
10	50
20	70
30	100
45	240
60	360

From these results, we see that the light possesses bactericidal action, and as the distance increases, the intensity decreases, but there is no constant ratio between the two. The intensity of light decreases inversely as to the square of the distance from the sources; but in this case this rule does not follow. For comparatively long distances, however, this rule does apply. The error due to the short distance from the source of light is very great, for the light is almost entirely reflected. As the distance increases, a greater percentage of the light striking the water enters, and the results follow the rule. Of course, less light strikes the water at greater distances, but less is reflected. If we consider the results for the longer distances as being more accurate, the following would be the theoretical time sterilization.

Distance, in cm.	Actual time, secs.	Theoretical time, secs.
60	360	350
45	240	210
30	100	90
20	70	40
10	50	10
5	20	2.5

We see here that the results follow the theoretical for the longer distances.

The apparent decreasing of the depth of water, for longer distance, as the angle of incidence increased, would also decrease the time required.

Then, due to the light being to a great extent reflected at short distances, our results do not account for the great error entering in.

(b) On the penetrating power of the light.

(aa) In relation to the depth of water.

The water was placed in the containers at depths from 0.5 cm. to 25 cm., while the distance from the source of the light to the surface was kept at 10 cm.

Results—	
Depth of water, in centimeters.	Time, in seconds.
0.5	15
2.5	50
5.0	1,200
10	2,400
25	3,600

In the case of water 25 cm. in depth, at the end of one hour there was a decrease in the bacterial content, but the water was by no means sterilized.

From this table, we see that there is a rapid decrease in the penetrating power of the light with increase in the depth of water. The increase in the volume of the water would account for this to some extent, but would not explain the great decrease in the penetrating power. Bacteria become coagulated when exposed to the light,[4] and colloids absorb the ultra violet rays,[5] so perhaps this will help in the explanation.

(bb) In relation to turbidity.

Unfiltered sewage containing about 50,000 bacilli per cc. and filtered sewage 20,000 bacilli per cc., was placed in the separate containers at depth of 0.5 and 10 cc. at distance of 10 cm. from the light.

Results—	
Sewage unfiltered.	
Depth in cm.	Time, in seconds.
0.5	300
10	2,400 not sterilized
Sewage filtered.	
Depth, in cm.	Time, in seconds.
0.5	120
10	2,400

At the end of 40 minutes the unfiltered sewage, 10 cm. in depth, was not greatly affected by the light, while the filtered sewage at the same depth was sterilized. The unfiltered sewage was very turbid, so this shows that turbid waters are very difficult to sterilize. The absorption of the ultra rays by the colloids will explain this.[5]

(cc) In relation to interposed substances.

The polluted water was placed in different colored

[4] J. Gasbel—54,853.
[5] Compt. rend. 151, 677.

bottles and exposed to the light at a distance of 10 cm. At the end of an hour's exposure there was no appreciable decrease in the bacterial content of the water.

Bottles used were:

Arcadian ginger-ale bottle—dark yellow in color.

Clysmic water—dark yellow in color.

Salt mouth bottle—thick white glass.

Erlenmeyer flask—lab. flask.

Jena flask—lab. flask.

The fact that the water in the bottles was not sterilized by the light shows that certain interposed substances absorb the ultra violet rays.

Conclusion:

The light produced from the iron arcs contains sufficient ultra violet rays to sterilize polluted water in thin layers and at short distances from the source of light, in a short time. The light does not possess great penetrating power.

The above work was done in the laboratory at Carroll College, Waukesha, Wis., in the spring of 1911, under the direction of Prof. B. S. Hopkins.

A NEW SOURCE OF TURPENTINE SUPPLY.

A recent bulletin has been issued by the Department of Agriculture to the effect that careful tests by the department have proved that turpentine made from Western yellow pine can be put to the same uses as that produced from the long leaf pine of the Southern States. The forests of the latter are being so rapidly used up, that grave fears have been expressed let in the near future turpentine would no longer be available for use in the paint industry, but the enormous extent of the forests of the Western pine has apparently pushed back the period of the extinction of the turpentine industry indefinitely. It is true that owing to climatic difference, the flow of turpentine from the Western pine is less than that from the long leaf pine, and that economic problems relating to production and marketing yet remain to be solved, but the fact that another source of turpentine supply besides the Southern forests is available, will do much to reassure those who have been so fearful that we were coming to the end of our supply of an article which is so important in the paint industry.

The U. S. Civil Service Commission, Washington, D. C., will hold an open competitive examination for practical paper maker, for men only, on June 4, 1913. From the register of eligibles resulting from this examination certification will be made to fill a vacancy in this position in the Bureau of Standards, Department of Commerce, at a salary of $1,000 a year, and vacancies as they may occur in positions requiring similar qualifications, unless it is found to be in the interest of the service to fill any vacancy by reinstatement, transfer, or promotion.

THE SPECIFIC HEAT OF COAL AND ITS RELATION TO THE PRESENCE OF COMBINED WATER IN THE COAL SUBSTANCE.*

By HORACE C. PORTER and GUY B. TAYLOR.

The specific heat of coal is hardly capable of precise determination. Coal is a conglomerate of varying composition, unstable and easily subject to change by heat and by exposure to the air. Nevertheless, a determination of the specific heat is possible on a given sample with some degree of accuracy, and there may be determined also the influence of the character of the coal and the percentage of moisture on the specific heat.

When a coal is being heated, for any purpose, or when for no purpose it heats spontaneously, it passes through a range of temperature from 20° C., say, to 250° or 300° C. before it ignites, or before, in the absence of air, it begins to decompose rapidly by destructive distillation. During this preliminary heating of coal, whether it may be in a coke oven, gas retort, or gas producer or in the "green" coal layer of a fuel bed of a furnace, it is of interest and often of value to fuel engineers to know the quantity of heat communicated to the coal for a given temperature rise; i. e., its specific heat.

Solids have in general a much lower specific heat than that of water, metals in most cases less than 0.1 and sand, fire clay, porcelain or glass not far from 0.2. These solid substances thus require only 1/10 or 1/5 as much heat as is required by water, in order to raise their temperature a given number of degrees. Coal, we should expect by reason of its organic nature and its content of water, to have a higher specific heat than metals or clay. Bituminous coal, air-dry, proves to have, in fact, through the temperature interval 28° to 65° C., a value varying from 0.261 for the New River type to 0.370 for Wyoming sub-bituminous of 11 per cent moisture. The specific heat becomes greater at higher temperatures, that of the New River type for example being 0.354 between 177° and 227°. In Table I are given the results of the determination of specific heat made in this investigation.

The specific heat of coal has been given values by different authorities varying from .20 to .45, with usually no qualifying statement as to moisture content or character of the coal. As a matter of fact the moisture content affects materially the specific heat, and from the relationship between the specific heat of dry and undried coal may be deduced certain conclusions as to the form of combination of the water present.

Coal is essentially an organic material, the product of the degradation of cellulose and other plant tissues and contains, like most other materials of vege-

*Presented by permission of the Director, U. S. Bureau of Mines.

table origin, some water in a state of physical or chemical combination. When exposed to air of average humidity coal does not dry out, but assumes rather a state of moisture equilibrium at which there remains in the coal from one to sixteen per cent of moisture depending on the kind of coal and the humidity of the air. In other words, the vapor pressure of the moisture in coal does not reach the normal tension of water vapor until the amount present exceeds a certain percentage, and up to that percentage, therefore, the water present in coal does not exist as free superficial moisture. An experimental study of the vapor tensions of coals of different water content, bringing them to equilibrium over sulphuric acid of various dilutions, has confirmed these conclusions.[1]

By comparison of the specific heats of dry and undried coal, knowing the percentage of water present, the molecular heat of the water may be calculated. A coal from Franklin Co., Illinois, bearing 9.4 per cent water, has a specific heat of .337, while in the dry condition its value is .301. Following Kopp's law, the specific heat of the water present in this coal is $.337 - (.916 \times .301) = .730$ and its molecular heat, $\frac{.034}{.730} = 18 \times .730 = 13.1$. Similarly a Wyoming sub-bituminous of 11.0 per cent moisture has in the undried condition a specific heat of .339 and in the dry state .315, the specific heat of its water being thus $\frac{.359 - (.89 \times .315)}{.11} = .718$ and the molecular heat 12.9.

The molecular heat of the combined water in many hydrated salts has been determined by Kopp and others.[2] Some examples are given in Table II:

The molecular heat of the water in coal is evidently lower than that of free uncombined water and approaches that of the combined water of some crystallized salts. The conclusion therefore follows, in agreement with that drawn from the vapor pressure relationships, that the moisture of coal is in part physic-

TABLE I.—SPECIFIC HEAT OF DIFFERENT COALS.

$K = \frac{w\,dT}{w\,dt} m$ (k=specific heat, w=weight of water heated) water-equivalent of apparatus (14.1 grams), w=weight of substance, dT=rise of temperature in calorimeter, dt=fall of temperature in coal.

Expt. No.	Coal No. or substance.	W.	W.	dT.	dt.	k.	Temp. range.
39	9614 (New River)	229.5	45.0	1.95	37.6	.264	66.0-28.4°
41	9614 (New River)	238.6	40.0	1.56	36.0	.259	64.0-28.0°
45	9614 (New River)	206.7	40.0	1.74	34.4	.261	62.8-28.4°
49	384 (Pittsburgh)	215.6	40.0	1.85	34.8	.286	63.4-28.6°
50	384 (Pittsburgh)	204.8	39.1	1.71	31.8	.282	60.8-29.0°
51	384 (Pittsburgh)	209.4	40.0	1.80	32.9	.286	61.8-28.9°
52	384 (Pittsburgh)	223.1	40.0	1.67	32.2	.289	61.6-29.4°
27	48 (Illinois)	236.8	40.0	2.07	35.3	.347	64.4-29.1°
28	48 (Illinois)	246.8	40.0	1.90	35.0	.335	64.4-29.4°
29	48 (Illinois)	249.5	40.0	1.98	36.4	.339	64.4-28.0°
32	48 (Illinois)	220.9	40.0	2.16	34.7	.344	63.0-28.3°
36	48 (Illinois)	218.8	39.9	2.04	33.6	.333	62.5-28.9°
37	48 (Illinois)	232.6	34.9	1.77	34.4	.345	62.9-28.5°
59	48 (in toluene)[1]	122.5	35.0	2.97	31.4	.331	61.5-30.1°
61	48 (in toluene)	123.3	28.8	2.56	32.0	.342	61.0-29.0°
72	575 (Wyoming)	209.6	30.0	1.97	36.2	.376	63.9-27.7°
73	575 (Wyoming)	232.2	40.0	2.40	37.2	.374	63.4-26.2°
74	575 (Wyoming)	224.2	26.5	1.71	38.5	.375	64.2-25.7°
66	575 (in toluene)	123.8	30.0	2.96	32.9	.371	62.2-29.3°
67	575 (in toluene)	123.2	25.0	2.47	35.8	.361	63.2-29.4°
76	575 (in toluene)	121.7	50.0	3.11	36.2	.557	62.4-26.2°
62	48 (dry)[2]	123.3	30.0	2.46	33.4	.302	62.8-29.4°
63	48 (dry)	122.8	30.0	2.44	33.1	.301	62.6-29.5°
64	48 (dry)	122.3	28.0	2.30	35.5	.300	62.7-29.2°
68	575 (dry)	122.6	30.0	2.62	34.5	.312	63.8-29.5°
69	575 (dry)	124.1	25.0	2.26	35.2	.318	64.3-29.1°
15	Copper[3]	218.5[3]	103.1	1.58	35.9	.0933	64.6-28.7°
19	Copper	227.3	101.7	1.49	35.7	.0933	64.8-29.1°
17	Copper	227.4	102.2	1.53	36.5	.0933	64.7-26.2°
41	Copper	196.3	101.3	1.70	35.3	.0933	63.5-28.2°
14	Lead (.0310 at 17°-100°)[4]	237.1	284.6	1.35	36.4	.0308	64.5-28.1°
3	Same	210.1	356.0	1.64	35.7	.0305	64.3-28.6°
23	Marble (.206 at 0°-100°)[4]	235.5	60.0	1.88	36.8	.201	64.8-28.0°
24	Same	232.6	50.0	1.68	36.4	.202	64.8-28.4°
33	Jena Glass (.2182 at 18°-99°)[4]	209.8	44.5	1.35	33.1	.192	61.5-28.4°

[1]Water equivalent of toluene = Wgt. used × .421.
[2]Using toluene.
[3]Used as standard, to determine water equivalent of calorimeter, assuming specific heat as .0935. In exp. 15, 214.3 grams of water were used, in No. 19, 213.3; in No. 17, 212, and in No. 41, 113.4 grams.
[4]Values taken from Landolt & Bornstein Tabellen.

[1]Acknowledgment is due to Mr. O. C. Ralston for the greater part of the experimental work on vapor pressure of coal.

[2]Kopp, Phil., Trans. London, 135, (I), 71; (1865); Schottky, Zeit. Phys. Chem. 64, 415; (1908).

ally or chemically combined. Still further experimental evidence of the presence of combined water was incidentally encountered in developing the method for determination of specific heat. In attempting to determine the value for dry coal by the method of numbers, adding the heated coal to water in a calorimeter, so large a rise of temperature resulted that the specific heat appeared to be much greater than that of the undried coal. Since the moisture in coal calorimeter, since toluene was found to have almost no calorific action on the dry coal. That the calorific action of water on dry coal is due to chemical or physical combination becomes highly probable in the light of the two other phenomena previously mentioned which lead to the same conclusion, viz.: the low vapor pressure and the low molecular heat of the water in coal.

Experimentally, the determinations of specific heat

TABLE I-A.—SPECIFIC HEATS OF COALS AT HIGHER TEMPERATURES.

(Water-equivalent of calorimeter 14.1 grams.)

Expt. No.	Coal No. or substance.	W.	W.	dT.	dt.	k.	Temp. range.
99	Copper	207.7	45.0	2.03	100.4	.0933	125.5-25.1°
102	Copper	209.1	15.0	2.11	103.8	.0945	129.5-25.7°
98	384	216.7	10.0	1.48	106.1	.302	131.0-24.9°
100	384	224.1	12.0	1.73	105.1	.307	130.0-24.9°
101	384	226.6	11.0	1.63	104.6	.315	130.0-25.4°
105	381	193.2	10.0	1.68	104.6	.310	130.0-25.4°
103	9614	222.7	11.0	1.48	103.3	.290	128.0-24.7°
104	9614	205.1	10.0	1.43	102.3	.287	127.5-25.2°
106	9611	191.5	9.5	1.51	106.2	.287	132.0-25.8°
88	Copper	340.2	41.0	1.73	151.3	.0948	176.0-24.7°
90	Copper	324.5	37.0	1.67	155.9	.0938	181.0-25.1°
92	Copper	315.1	36.7	1.68	154.1	.0936	179.0-24.9°
89	384	313.1	10.0	1.57	153.3	.318	176.5-21.2°
96	384	320.9	10.0	1.48	148.0	.321	172.7-24.7°
93	9614	314.5	12.0	1.76	154.5	.298	179.0-24.5°
94	9614	308.0	10.0	1.49	151.5	.305	176.0-24.5°
108	Copper	296.9	20.0	1.24	195.4	.0942	220.7-25.3°
110	Copper	296.9	30.0	1.90	198.3	.0948	223.7-25.4°
107	384	330.5	6.0	1.22	200.1	.332	225.5-25.4°
109	384	307.1	8.0	1.73	199.8	.332	225.5-25.9°
111	9614	314.1	8.0	1.64	204.6	.315	229.7-25.1°
113	9614	278.0	9.0	2.03	201.0	.312	226.6-25.6°

TABLE I-B.—SUMMARY OF AVERAGE VALUES OBTAINED FOR THE SPECIFIC HEAT OF COAL AT DIFFERENT TEMPERATURES.

					Calculated values		
Coal.	63-28°	130-25°	177-25°	227-25°	130-63°	177-130°	227-177°
9614	.261	.288	.301	.314	.303	.329	.354
384	.286	.308	.320	.332	.321	.347	.368
48	.330	...	...	...	...	...	...
48 (dry)	.301	...	...	...	...	...	...
575	.370	...	...	...	...	...	...
575 (dry)	.315	...	...	...	...	...	...

should increase its specific heat on account of the higher specific heat of water even when in combination, the discrepancy was at once attributed to some inherent error of the method. This error was found to lie in the development of heat by the physical or chemical action of water on the dry coal. Dry coal and water carefully brought to the same temperature in separate vessels were mixed in a calorimeter and the development of heat measured. The results given in Table III show in case of Wyoming coal a heat development of 20.0 calories per gram, so that in the specific heat determination using 30 grams of this coal dry, and mixing it with water, there were developed 600 calories as heat of combination, affecting thus in no small degree the result of the specific heat determination.

The correct values for dry coal were therefore determined by using toluene in place of water in the were carried out as follows: Early in the work an attempt was made to use a method depending upon the addition by electrical means of a definite amount of heat energy to coal suspended in water, noting the rise of temperature which resulted in the coal and water mixture. Since, by this method, using a weight

TABLE II.

Substances.	% H_2O.	Specific heat.	Molecular heat of water present.
$CuSO_4 \cdot 5H_2O$	36.1	.269	8.6
$CuSO_4$ (Anhydrous)	....	.151	....
$MgSO_4 \cdot 7H_2O$	51.2	.407	10.6
$MgSO_4$ (Anhydrous)	....	.216	....
$BaCl_2 \cdot 2H_2O$	14.7	.151	9.1
$BaCO_3$ (Anhydrous)	....	.090	....
$MnSO_4 \cdot 5H_2O$	37.1	.407	14.1
$MnSO_4$ (Anhydrous)	....	.182	....
Coal 48 (Ill.)	8.1	.337	13.1
Coal 48 (dried)	....	.301	....
Coal 575 (Wyo.)	11.0	.309	12.9
Coal 575 (dried)	....	.315	....

of coal a little more than one-tenth that of the water, the total energy change of the system was 30 times that of the coal, the experimental error was magnified 30-fold when referred to the coal. Thus, in order to obtain an accuracy of 3 per cent in the final result, an accuracy of 0.1 per cent was required in the experiment. This degree of precision being scarcely practicable, the simpler method of mixtures was resorted to, whereby it was possible to effect a comparatively large energy change in the coal itself. The coal was heated to a temperature about 37° above that of the calorimeter, and was subjected thus, on mixing with the water of the calorimeter to a change of temperature of about 34° while the water changed less than 3°. The total energy change in the coal was equal to that in the balance of the system or, in other words, one-half of that of the entire system, so that the experimental error became magnified only two-fold when referred to the coal. The determinations were easily checked with a maximum deviation of 2 per cent from the mean (see Table I).

TABLE III.—HEAT OF COMBINATION, DRY COAL AND WATER.
(Water equivalent of calorimeter+water=48 grams.)

Expt. No.	Coal. No.	Weight of coal.	Weight of dried coal.	Moisture %.	Moisture in dried coal.	Temp. rise %.	Total calories.	Calories per gm. original coal.	Calories per gm. dried coal.
2a	43	15.0	11.93	20.4	1.0	4.31	207	13.8	17.3
2b	43	15.0	12.00	20.0	1.4	3.97	191	12.7	15.9
3a	43	15.0	11.80	21.6	0	4.92	236	15.7	20.0
3b	43	15.0	11.80	21.3	0.1	4.79	230	15.3	19.5
4a	43	15.0	14.43	3.8	17.6	.40	19.2	1.3	1.4
b	43	15.0	13.98	6.8	14.6	.69	33.5	2.2	2.4
c	43	15.0	13.31	11.3	10.1	1.21	58.0	3.9	4.3
d	43	14.5	12.50	14.0	7.4	1.79	86.0	5.9	6.8
e	43	15.0	12.09	19.4	2.0	3.55	170.4	11.4	14.1
f	43	15.0	11.92	20.5	.9	4.36	209.0	13.9	17.5
5a	43	....	14.00	....	16.7	.36	17.3	.....	1.2
b	43	....	14.00	....	14.8	.45	21.6	.....	1.5
c	43	....	14.00	....	14.8	.46	21.7	.....	1.5
11	43	....	14.00	....	15.1	.53	25.4	.....	1.7
7a	48	15.0	14.70	1.98	6.7	0.16	7.7	0.51	.52
b	48	15.0	14.43	3.79	4.9	.20	9.6	.65	.66
c	48	15.0	14.23	5.18	3.5	.36	17.3	1.15	1.22
d	48	15.0	14.04	6.38	2.3	.58	27.8	1.85	1.99
e	48	15.0	13.86	7.60	1.1	.66	31.7	2.11	2.30
f	48	15.0	13.75	8.32	.4	1.00	51.8	3.45	3.80
g	48	15.0	13.70	8.62	.1	1.21	58.1	3.90	4.20
8	48	15.0	13.77	8.25	.5	.98	47.0	3.13	3.33
9a	384	15.0	14.82	1.20	.6	.12	5.7	.39	.40
b	384	15.0	14.78	1.44	.4	.18	8.6	.57	.58
10a	9614	15.0	14.84	1.05	.1	.0	.....	.....	.0
b	9614	15.0	14.85	.98	.2	.08	.....	.....	.....

The calorimeter vessel was a tinned can of 400 cc. capacity resting on a cork in a large Dewar vessel, more than twice the height of the can. The Dewar tube rested in a jar of water at room temperature. A revolving propellor-shaped stirrer was used, attached to a glass rod and operated by a water motor at 150-200 revolutions per minute. The thermometer was a calibrated Beckman of good quality. For introducing the heated coal or other substance a wide glass tube—about ¾-in. diameter—was inserted from above so as properly to direct the fall of the coal, yet not touch the calorimeter can, stirrer, or liquid. The coal was sized between 10 and 20 mesh so as to fall easily through the tube and mix with the water.

For the heating of the coal before mixing, a double walled cylindrical glass vessel was used, between the walls of which a little methyl alcohol was kept boiling by a platinum coil electrically heated. The inner cylinder contained the coal, supported near the bottom by a metal plate which could be quickly pushed out allowing the coal to drop. A calibrated thermometer graduated in tenths of a degree rested in the center of the coal in the inner tube. When the coal had reached a constant temperature, the heater was brought over the calorimeter and the coal dropped.

In order to correct for radiation, temperature readings were taken at one-minute intervals during a 5-minute period before the mixing and during a 10-minute period after the maximum temperature had been reached. The cooling correction was applied by the well known Regnault method common in calorimetric work. The temperature rise due to the mixing reached its maximum usually in 3 minutes, and the cooling correction applied did not exceed .05 degree or about 2 per cent of the total rise.

The amount of water used in the calorimeter was 200-230 grams, the water equivalent of the apparatus was determined by runs with pure copper shot assuming the specific heat of pure copper at 25°-65°, to be .0933—an average of Naccari's values at 17° and 100°, and based also on Schmits' value (.0066) at 20°-100°.[3] On this basis the specific heat of a

[3]Naccari; Atti di Torino, 25, 107; (1868), Schmitz, Proc. Roy. Soc. 72, 177; (1903).

number of other substances was determined in the apparatus, comparing the values obtained with those given by other authorities, and the agreemnt was found in most cases good (see Table I).

Determinations were made upon four coals of widely varying character, two being high grade Eastern coals of low moisture content and two from the interior and western fields comparatively high in moisture content. They were used both in the air-dry and the moisture-free condition, but not in the unstable moist condition as received from the mine. The moisture-free samples were prepared by drying 100 grams, 10-20 mesh size, for two hours in a 30 mm. vacuum at 100° C.

For the determinations upon dry coal toluene was used in place of water. The water equivalent of the apparatus containing toluene was redetermined with copper. Some of the determinations made on undried coal in water were repeated in toluene and the agreement was good (see Table I).

The specific heat of the two coals (9.614 and 384) was determined at higher temperature ranges, viz., 130°-25°, 177°-25°, and 227°-25° (see TableI-A). For preheating the coal there was used a mercury bath heated to the desired temperature and a double-walled glass test tube for transferring the heated coal from the bath to the calorimeter. A thermometer was imbedded in the coal while it was being heated, and temperature read immediately before dropping the coal, correction being made for the exposed stem of the thermometer. About 10 grams of coal were used. The determinations were checked by copper at each temperature. On account of the difficulty of avoiding loss of moisture during the preliminary heating, no determinations were attempted on the Illinois and Wyoming coals at these higher temperatures. Having the average specific heat between 25° and 65° and the average between 25° and 130°, it is possible to calculate the average value between 65° and 130°; similarly also those between 130° and 177° and between 177° and 227° (see Table Ib).

TABLE IV.—DESCRIPTION OF COALS.

Lab. No.	Source.	Loss on air drying.	Analysis of air-dried sample. Moisture.	Volatile matter.	Fixed carbon.	Ash.
9614	Sun Mine, Fayette Co., W. Va. (New River field)	2.0	1.80	20.30	72.36	5.46
384	Schoenberger Mine, Baird Sta., Washington Co., Pa. (Pittsburgh bed)	1.4	1.20	34.50	58.44	5.86
48	Dering No. 11 Mine, W. Frankfort, Ill. (Franklin Co.)	*	8.40	54.96	48.23	8.42
575	Dietz No. 2 Mine, Sheridan Co., Wyo. (Sub-bituminous)	14.0	11.00	38.56	40.24	10.20

HEAT EVOLVED BY MIXING DRY COAL AND WATER.

For approximate determination of the heat evolved by mixing dry coal with water, 12-15 grams of the dry or partially dried coal of known moisture content was mixed with 40 cc. of water in a nickel calorimeter cup, and the mixture stirred by hand with the thermometer. The nickel cup rested on a cork in a deep Dewar vessel standing in a water bath. The thermometer was a calibrated Beckman. The coal, before mixing with the water, was contained in a glass tube with movable bottom, and was brought to the temperature of the water by holding in an air bath of the right temperature until a thermometer inbedded in the coal became constant at the point desired. The tube of coal was then brought over the calorimeter cup and the coal dropped into the water by moving aside the supporting disc at the bottom.

With the Wyoming Coal the maximum temperature was reached in 2-5 minutes, while with the Illinois coal the action was slower requiring from 8 to 12 minutes to produce a maximum temperature. The cooling correction was small.

The water equivalent of the apparatus was determined by mixing the portions of water of different temperatures, and was also calculated roughly from the known specific heats of the materials. An average value of 4.5 grams was used. To this was added, in order to obtain the total heat capacity of the system, the weight of water used and an approximate value for the water equivalent of the coal used. The latter value however involved an uncertainty due both to the change in specific heat of the coal by combining with water and to the conversion of part of the free water into combined water of a different specific heat. The two errors tend to balance each other and the resultant error was probably not large. Taking 12.5 grams of dry coal, its water equivalent was assumed to be 3.7 grams with a probable error of 0.3 gram or less than 1 per cent of the total heat capacity.

The coals used were the same as in the specific heat determinations except that in place of the air dried sample No. 575, an undried sample from the same mine, No. 43, containing 21.42 per cent moisture was substituted in order to observe the full effect of saturation of the coal substance with water. The coals were ground so as to pass a 20-mesh sieve and be retained on a 40 mesh. The moisture in them, determined by the official method was as follows:

		Per cent.
No. 43	Sheridan Co., Wyo	21.42
No. 48	Franklin Co., Ill	8.70
No. 384	Pittsburgh bed, Pa	1.78
No. 9614	New River district, W. Va	1.15

There is an error due to oxidation in the official method for moisture determination, rendering the results for moisture content, especially in case of the Illinois and sub-bituminous Wyoming types, appreciably lower than the true percentage. Consequently no precise comparisons of heat development with moisture content can be made from the results in Table 3, since the moisture figures are not strictly ac-

*Not determined; sample allowed to dry at 20°—25° in air of room.

curate. The samples used in the determinations were prepared as follows:

Exp. 2, 3, and 4 (Coal 43): 15 gram portions dried for varying periods of time over sulphuric acid at 2 mm. pressure, determining loss of moisture by loss of weight and the moisture remaining by difference between this loss and the total moisture (official method).

Exp. 5: 15 gram of coal saturated with water and then air dried at room temperature.

Exp. 11: Original coal air dried at room temperature 72 hours.

Exp. 7: Coal 48, dried in vacuo over sulphuric acid as in Exp. 4.

Exp. 8: 15 gram portion in weighing bottle oven dried at 105° 1½ hours in current of air.

Exp. 9 and 10: Coals 384 and 9614 dried in vacuo as in Exp. 4.

Coal has a specific heat varying according to the character of the coal substance and the amount of moisture, both free and combined, which the coal contains. The water content affects the specific heat in such manner as to indicate that up to a certain percentage the water is present in a state of physical or chemical combination. Other facts, viz., the low vapor tension of the water in coal and the development of heat on moistening dry coal, support this theory. The heat development by the moistening of dry coal may contribute appreciably to the spontaneous heating of some coals in storage.

Concerning the discovery of coal in the Antartic regions visited by the Shackleton and Scott expeditions, Prof. D. W. Edgeworth David, professor of geology and physical geography in the University of Sydney, is quoted in the Australian press as saying: In reference to the scientific discoveries of Scott's party there can be no doubt they will prove of immense interest and importance. In the first place it is stated that a good collection has been obtained of fossil plants associated with the seams of coal discovered by Shackleton at Buckley's Island, at the head of the Beardmore Glacier. Frank Wild, of Shackleton's party, was the actual discoverer of seven seams of coal outcropping in a great cliff face of sandstone and shale. The thickness of these seems was 7 feet, inclusive of a few clay bands, and Wild chopped small specimens of the coal out with his ice ax. These have been analyzed in Sydney and show the coal to be of workable quality. It is almost certain that this coal field will prove to be perhaps one of the largest of the unworked coal fields of the world, as it has been traced now through the further researches of Capt. Scott's geologists, Messrs. Griffith, Taylor, and F. Debenham, to a point about 650 miles north of the head of the Beardmore Glacier.

Austrian hop production last season was 44⅓ million pounds, against 19 million in 1911 and 36½ million in 1910.

IMPROVING THE QUALITY OF ALUMINUM.*

Aluminum is a very useful metal, although it is so comparatively new to us; but like other metals it has its faults, which we seek to neutralize by alloying it with other materials, since the action of heat upon it does not effect any desirable changes therein, as is the case with steel.

Among the experiments that have been made in the way of alloying are those with cobalt, the results of which have not become very generally known, and which are especially interesting when the action of this alloy is increased by the addition of tungsten and molybdenum.

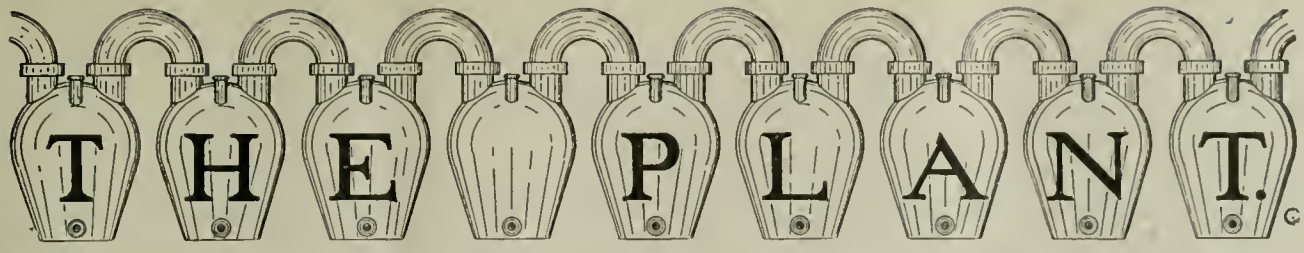
Scientific researches into the chemical relation of aluminum and cobalt in alloy form go to show that those two metals are so to say soluble in each other. Of the various alloys that have been made and studied, the one with the least percentage of cobalt had ⅓ of this metal therein; its solidifying point being somewhat above 100° C. Between this compound and aluminum there is a "eutechtic" containing only 0.5 per cent of cobalt, and having a melting point lower than that of pure aluminum. There is also in the curve showing the melting points of the aluminum-cobalt alloys, a decided kink at the point corresponding to 20 per cent of cobalt.

With 9 to 12 per cent of cobalt there are obtained alloys that are almost free from bubbles, although the fracture is somewhat coarse and crystalline; and although the tensile strength is not much above that of pure aluminum the alloy is more readily turned and polished, etc., and much more resistant to atmospheric influences. These alloys are still quite light and much more workable than pure aluminum. The lack of tensile strength is due to the coarse crystalline fracture, but this may be improved by the addition of tungsten (which the Germans call "wolfram") and molybdenum, so that by the help of these an alloy with but a small percentage of cobalt has three times the tensile strength of aluminum, and is also malleable and ductile. These alloys run about 0.8 to 1.2 per cent tungsten, 8 to 10 per cent cobalt, the rest aluminum.

The more cobalt these alloys contain, the less readily can they be rolled, but the greater their tensile strength; so that those with high cobalt percentage are better for castings, the poorer ones better for forging and rolling. The alloys of molybdenum, cobalt and aluminum run from 0.6 to 1 per cent molybdenum, 9 to 10 per cent cobalt, the rest aluminum; these follow about the same general rules as those of wolfram, cobalt and aluminum, except in the matter of hardness, in which they are inferior to the corresponding tungsten-cobalt alloys.

Rubber shipments from Federated Malay States in January totaled 4,772,800 lbs.—100 per cent increase over January, 1912.

*From The Metal Industry.



THE ELECTRIC FURNACE IN THE PRODUCTION OF IRON FROM ORE.*

By D. A. LYON.

As is well known, the electric furnace, under favorable circumstances, may be used in the iron and steel industry for the production of metal from the ore, and later for the refining of this same metal into the grade of steel desired.

It was pointed out by the Canadian Commission in their report of 1904 that the prime prerequisite for the use of the electric furnace in the reduction of iron ores is cheap electric power. The large amount of experimental and practical work which has been done since that time has only emphasized this fact. The electric furnace, therefore, has not been developed as a competitor of the blast furnace, but, as is the case in Norway and Sweden, for the purpose of keeping alive an industry which finds itself confronted by conditions unfavorable to a continuation of blast furnace practice, due to the increased cost of charcoal; or for the purpose of making possible the development of the iron industry, as is the case in California, where the iron industry has never been developed, due to the cost in that section of the country of both charcoal and coke.

In each country, considerable experimental work was first done, and then the furnace was tried out on a commercial scale. As was to be expected, the problems which presented themselves at the outset of the work were not solved at once, and there are still problems which are awaiting a more satisfactory solution than has so far been attained, but satisfactory progress is being made in this direction. That the electric iron ore reduction furnace has entirely passed the experimental stage is evidenced by the situation in California and Scandinavia.

THE SCANDINAVIAN PRACTICE.

Due to the large number of articles descriptive of the work in Sweden, which have previously appeared, it will not be necessary in this connection to do more than to refer to them and to state briefly the status of the electric reduction furnace in Scandinavia at present.

As a result of the successful operation of the furnace at Trollhättan, three other iron electric reduction furnaces are now being operated in Sweden, which, together with the furnace at Trollhättan, represent a total of 12,000 hp. that is being used for electric reduction furnace work in that country; in Norway there is one 3,500-hp. furnace in operation and one 3,500-hp. and three 3,000-hp. furnaces in the course of construction, while in Switzerland one of 2,500 hp. is being built.

As was likewise pointed out in the September, 1912, number of *Metallurgical and Chemical Engineering*, the Uddleholms Company, at Hagfors, Sweden, are increasing their electric furnace installation by the addition of three more furnaces, and will probably substitute electric smelting altogether for their blast furnace work. It is also a significant fact that the plant at Trollhättan, which was built by the Jern-Kontoret, of Sweden, purely for the purpose of determining the feasibility of attempting to reduce iron ores in an electric furnace, has been sold by the Jern-Kontoret to the Degerfors Iron Company, and will be worked by the latter company as a commercial proposition from now on. The Degerfors Company is an old established company, who make very high grade material, and so it is not a case of a new concern taking up with a new venture, but one with long experience in the business, who have had ample opportunity to carefully study the feasibility of electric reduction furnace work under the conditions prevalent in Sweden, and who, as a result of their study, have satisfied themselves that the electric furnace will meet their requirements. In fact, the old saying, "the proof of the pudding is the eating thereof," would seem to apply as regards the use of the electric reduction furnace in Sweden.

If a study be made of the drawings of those furnaces which have been tried experimentally, it will be noted that in most of them an attempt was made to construct a furnace somewhat similar to a blast furnace, and to introduce the electrodes into the stack of this furnace at that point where the tuyeres are located in the former. All those who tried this soon learned that it was practically next to impossible to maintain the furnace walls adjacent to the electrodes. There was thus evolved, as a matter of necessity, the type of furnace construction which was finally adopted by the Swedish experimenters, and such as is shown in Fig. 1. By referring to the same, it will be noted that the furnace consists of two separate parts, namely, the crucible or hearth, superimposed above which is a shaft or stack. One of the most serious difficulties that had to be overcome in the perfecting of the electric reduction furnace was the maintenance of the crucible walls and roof. Such a construction as shown in Fig. 1 solved the difficulty as it meets the necessary prerequisites, namely, keeping the end

*From Metallurgical and Chemical Engineering.

of the electrode dipping into the charge as far removed from the side wall as possible, and, second, keeping that part of the crucible out of contact with the charge at the point where the electrode enters the crucible. The reason for having to observe these precautions is due to the fact that the heat is excessive at that point where the electrode comes in contact with the charge, and hence this point should be as far removed as possible from both the side walls

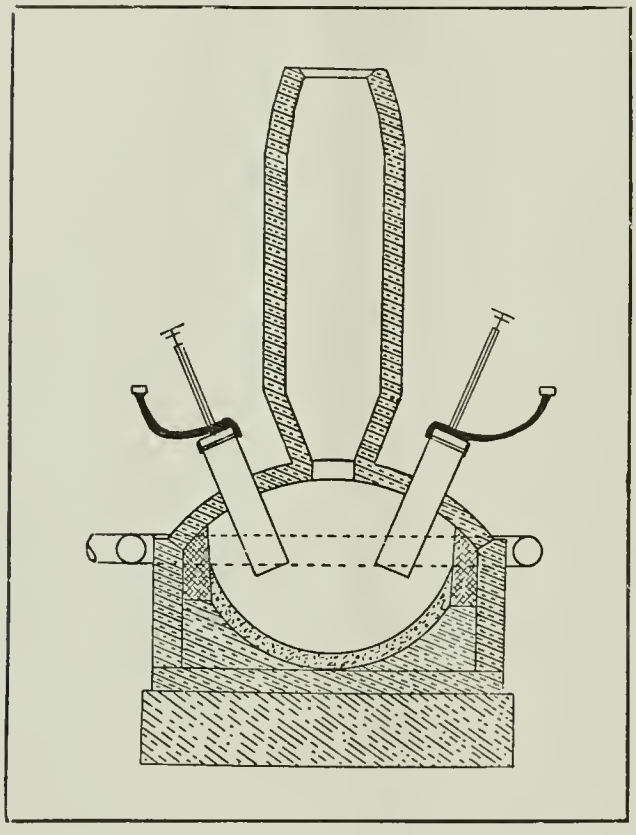


Fig. 1—Section of Swedish Type.

and roof of the crucible, in order to prevent the destruction of same through fusion.

The Electrode Problem.—When the demand was first made upon the manufacturers of electrodes for large electrodes of, say, 20 in. in cross section and 72 in. long, they experienced considerable difficulty in furnishing an electrode which would not go to pieces when put into commission. This caused considerable loss and annoyance to those attempting electric reduction and steel furnace work. Even if the electrode did not go to pieces, as soon as one-half to two-thirds of the same had been consumed it became too short for further use, and those unused portions represented a considerable item of expense. At the present time it is not only possible to obtain quite satisfactory electrodes, but also to avoid the waste above mentioned. This is done by joining a new electrode to the butt end of an old one, as is done at Trollhättan and at various other places.

So far, our remarks have been applicable alike to the California practice and to the Scandinavian practice. It will, however, at this point, be necessary to discuss each practice separately, as they are at the present time radically different from each other. In order to understand the situation more clearly, it may perhaps be well to briefly outline the development of the electric reduction furnace as it has taken place in California.

THE DEVELOPMENT OF THE ELECTRIC REDUCTION FURNACE IN CALIFORNIA.

For 25 years or more a company known as the Shasta Iron Co. has owned a deposit of magnetite, located about seven miles from the mouth of the Pitt river, in Shasta county, California. This ore is a very pure magnetite, having on an average the following percentage composition:

Fe	69.90
(Fe_3O_4 89.4; Fe_2O_3 7.3)	
MgO	0.10
MnO	0.18
SiO_2	2.40
P	0.011
S	0.009

Although at one time or another the Shasta Iron Company has planned to make pig iron from this ore, nothing definite was done in regard to the same until the summer of 1906. At this time the possibility of smelting this ore by electricity was brought to the attention of Mr. H. H. Noble, president of the Northern California Power Company. Due to Dr. Heroult's connection with the experimental work which had been done at Sault Ste. Marie, he was commissioned to construct a plant for the purpose of treating the ores above mentioned. The place selected was at a point on Pitt river, near the mines. This place was named Heroult, and is still known by that name.

In July, 1907, the first furnace having been completed, experimental work was begun. This furnace was a 1,500-kw., three-phase furnace of the resistance type. It was soon found that the type of furnace first used presented mechanical difficulties which made its commercial use impracticable, and so it was closed down. A sketch of this furnace is shown in Fig. 2. In construction the crucible resembled a long elliptical-shaped iron box. The bottom was made of heavy cast-iron plates, into which had been cast cast-iron lugs or pins, and upon the iron plates was tamped a carbon bottom made of carbon paste. The bottom plates were connected with the bus bars in such a manner as to form a neutral in the three-phase system.

The electrodes passed through the roof, as shown in the sketch. They were suspended from copper holders which were water-jacketed. The charge was fed into the crucible through the pipe (*B*), an the gases from the crucibles passed up around (*B*) into (*A*), the idea being to thus preheat the charge in (*B*) by burning the gases around (*B*), air being admitted for that purpose through slots in the outer pipe just above the roof of the crucible. These pipes, however, proved too small, and the charge in them became so hot as to hang, and so they had to be done away with. It was also found impossible to maintain a roof over the crucible, and so the furnace was finally operated as an open-top furnace. Several tons of A

No. 1 foundry iron were made in this furnace, and later it was used for making ferrosilicon, but was finally closed down and removed in order to make room for the type of furnace subsequently adopted. After the closing down of this furnace, experimental work was conducted in a 160-kw. single-phase furnace, and from the results obtained in this furnace and its methods of operation a 1,500-kw., three-phase furnace was designed and built. This furnace was practically the same in construction as is the furnace shown in Fig. 1. In other words, there was developed simultaneously in Sweden and in California a similar type of furnace, although neither the Swedish inventors nor those engaged in the work in California knew of the other's work. The development of this type of furnace was continued until the spring of 1911. At that time, acting upon the advice of the consulting engineer then in the employ of the Noble Electric Steel Company, a radically different type of furnace was constructed. The object aimed at in the new design of furnace was to secure one which would be as easily controlled, so far as the regulation of the nature of the charge was concerned, as is the present open-hearth steel furnace. This furnace was not a success.

Another type was then hit upon, and this type has since been developed into a commercially successful furnace. The furnaces shown in each are quite similar, but in a recent article descriptive of the plant of the Noble Electric Steel Co. it is stated that "this resemblance is only general."

Electric Iron Reduction Furnace in California.—The following information in regard to this furnace and its operation has been furnished the writer by the secretary of the Noble Electric Steel Co., and is chiefly taken from a recent article by R. W. Van Norden on "Electric Iron Smelting at Heroult, Cal.," published in the *Journal of Electricity, Power and Gas*, Nov. 23, 1912.

The furnace is housed in a heavy steel frame building, covered with corrugated-galvanized iron. It is rectangular in shape, 120 ft. long and 75 ft. wide, and has a height of about 60 ft. The building is in two sections or bays divided by a line of columns. The more southerly of these is the pouring floor, on which the pigs are cast. Throughout this bay is operated a 50-ft. Northern Engineering Company traveling crane. This is electrically operated and has two hoists, one of 20 and the other of 5-ton capacity. A Cleveland Electric Controller & Manufacturing Co. lifting magnet, having a capacity of 2,000 lbs., is used in picking up the pigs. This magnet will lift about 1,000 lbs. of hot pigs.

The bay to the north of the center columns is given to the electric furnaces, their transformers and the necessary control. While but one furnace, having a capacity of 18 tons of pig iron per twenty-four hours, is at present in use, two more of slightly greater capacity are practically completed. There is space reserved, and it is intended to immediately construct three more, thus bringing the total number of furnaces in this building to six.

The Furnace.—The crucible is contained in a steel shell 27 ft. long, 13 ft. wide and 12 ft. high. The shell is so lined with refractories that the upper half of the box is rectangular, but in the lower half the sides taper toward the center of the foundation, and the ends slope toward the middle, to facilitate the flow of the molten bath, when the furnace is tapped. The tap hole is in the center and front of the crucible. The roof of the furnace is arched, and opening into the same are five stacks through which the charge is conducted into the crucible. In the four spaces between the stacks at the center of the dividing arches are inserted the graphite electrodes. The electrode jackets and the arched roof are water-cooled. The stacks or pipes through which the ore is charged are 24 in. in diameter and extend upward to a distance of 15 ft. from the roof of the crucible. These stacks are used only for the purpose of charging, no reduction being attempted in them. A charging platform is built along the top of the stacks and carries a track which runs to the mixing platform. Dump cars with the charges are run on the charging platform and dumped directly into the stacks. Except when receiving a charge, the stacks are closed with a tight-fitting cap.

The Electrodes.—Graphite electrodes are used. They are cylindrical in form, 12 in. in diameter and 4 ft. long. The upper end has a tapered male-threaded

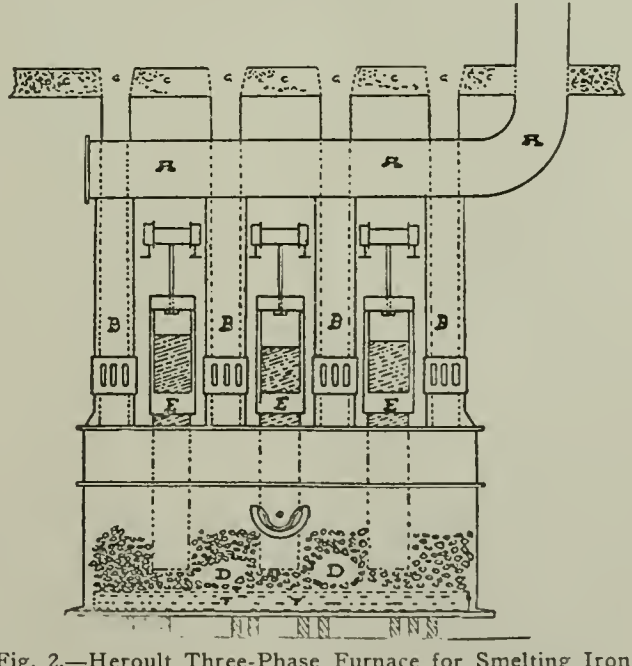


Fig. 2.—Heroult Three-Phase Furnace for Smelting Iron Ore.

nipple, while the lower end has a corresponding socket with a female thread. As the electrode is fed into the charge, a new one may be fastened to it, making a continuous feed.

An electrode lasts in continuous operation thirty days. Occasionally an electrode breaks in the fur-

nace. This was formerly a serious matter and caused considerable delay and annoyance in the operation of the furnace. It was hard to determine just where the break had occurred, although it was generally at the threaded joint. A novel means has been devised by which the furnace men are now able to ascertain whether an electrode is broken or not. A bar is driven into the furnace opposite the electrode, through one of the several peep holes, and at the same time the electrode is tapped on top with a hammer. The man on the bar simply listens for the tapping. The tapping is then done on the bar, and the man on the top listens. A break may be accurately located in this manner.

Transformers.—In the rear of each furnace, and as close thereto as is possible, are the three service transformers, which supply three-phase current at from 40 to 80 volts to the electrodes. These transformers are oil-immersed and water-cooled, and have a capacity each of 750 kw. The low-tension connections to the electrodes consist of eight pieces of flat copper bar, ⅜ in. thick and 5 in. wide, bolted together. On the 2,400-volt primary side there are brought out eight current taps for voltage regulation.

These are taken to an oil-immersed, individual solenoid-operated switch group, which, with auto-transformer compensator, gives fifteen steps for voltage variation.

Electric Control.—Electric control is through a switchboard, there being a panel for each furnace. As the current and power-factor in each phase must be under observation at all times during operation, separate meters are installed in each phase. The requirements for one panel are three ammeters, three voltmeters, three wattmeters, three power-factor meters and three recording wattmeters. These are mounted across the panel in rows of three each. Under the first four sets named are three hand wheels to control the voltage variation, and under these three switches, which control the entire load, and still under these are the recording wattmeters.

For operating the voltage control and the main circuit breakers there is a 7½-kw. motor-generator set, comprising a 125-volt direct-current generator, directly connected to a 10-hp. induction motor. This set has a small panelboard mounting a circuit breaker, ammeter, voltmeter, and two single-pole knife switches. The transformers, switches and control were supplied by the General Electric Co. In the event that line voltage should fall, or for any other cause the direct-current supply should become deranged, there is a National Storage Battery Co.'s set, having a capacity of 7½ kw., which may be instantly switched in, and thus prevent the furnaces from cutting out in the case of low voltage.

Operation.—In operation the furnace is continuous. After a period of eight hours the hearth contains a full bath of molten metal, and this is, therefore, tapped three times each day. Charging is done at regular intervals, and the current is not shut off at any time.

During the period of smelting the change in electrical conditions is interesting. At the beginning of the charge the power factor is almost unity. This gradually lowers as smelting continues, until with a full bath of metal a power factor of about 5 per cent is reached. If coke is used in place of charcoal, or if a mixture is employed, a different set of power factor conditions exists. By studying these conditions it is possible to know the exact condition of the charge by looking at the meters. The load is, of course, a function of the voltage, and with half voltage the load will drop one-quarter.

In charging, the ore cars are run on the mixing floor, which is at the same level as the charging floor. Cars with charcoal come into the lower part of the building and are hoisted on an electrically operated elevator to the mixing floor. Lime and quartz for flux are also brought in in cars, and each material is dumped into bins. The mixing is done in a car which is run on a platform scales. The charge is placed in layers, the proportions depending upon the tests made in the laboratory by the chemist. Following is a representative charge:

500 lb. iron ore (magnetite);
135 lb. to 150 lb. charcoal;
3½ lb. lime (well burned);
12½ lb. quartz.

COMPARISON OF THE CALIFORNIA AND SWEDISH FURNACE AND PROCESS.

As to the construction of the two types of furnaces, the difference is so apparent that no comment is necessary. As to the process, the California practice differs from the Swedish practice very decidedly in the following respects, namely:

1. No attempt at reduction in the stacks of the furnace.

2. Non-circulation of gases.

3. The use of limestone calcined outside the furnace.

In other words, the California practice is just the reverse of the Swedish practice, for in the latter they attempt reduction of the ore in the shaft of the furnace, they circulate a part of the gases escaping from the top of the shaft, and they do not use burned limestone.

Reduction in Shaft.—It would seem that the ideal condition in electric reduction furnace work would be to have the charge in such a condition as to only require melting by the time it comes in proximity to the electrodes. If this be done, the electric current is then only called upon to furnish the additional heat necessary to bring about the melting of the hot, previously reduced oxide. Of course, the heat for the reduction must come from some source, and its origin would be in the crucible, and as a result of the heat developed during the melting of the charge, but, as will be stated presently, the excess heat so developed can be transferred by the circulation of the gas to the

charge in the shaft and not carried away by radiation and an excessive amount of cooling water.

Gas Circulation.—In the Swedish practice, a portion of the gases rising from the top of the shaft are returned to the crucible and made to pass through the same and up through the charge in the shaft. This is done for the following reasons:

1 To cool the superheated brickwork.

2 To carry up through the stack a sufficiently large volume of gas which has been raised to a high enough temperature to bring about reduction in the stack.

As has been previously pointed out in this article, one of the most serious difficulties that had to be overcome in the development of the Swedish type of furnace was the destruction of the crucible due to local heating in the vicinity of the electrodes. Therefore, by returning to the crucible a portion of the gases resulting from the reduction of the ore, it is possible to prevent excessive local heating and at the same time to make use of the heat instead of wasting it. This matter has been the subject of much discussion, and has its objections, but the writer is of the opinion that its advantages in the way of economy of operation far outweigh its disadvantages. Perhaps it will in time be found practical not to use gas circulation in the electric iron reduction furnace, but, on the other hand, we believe that reduction previous to melting will be considered the proper practice, which means stack reduction, and the present California practice will not find application except in those instances where the local conditions warrant the same, as is the case at present. As has been pointed out, the present demand in California is for a soft grey foundry iron. The furnace now used gives that product, but this does not mean that such a construction and such a process are absolutely necessary for the production of such an iron. As a matter of fact, many tons of the same kind of iron were made at Heroult in a furnace of the Swedish type, and the Swedish inventors claim that it is possible to operate their type of furnace so as to reduce regularly an iron of the same character as is now produced at Heroult. They state, however, that in operating the furnace for this purpose the amount of electrical energy consumed per ton of pig produced is increased.

As to why the California type of furnace is better suited to the production of a soft grey foundry iron than is the Swedish type of furnace, it is probably due to the fact that reduction is performed solely by solid carbon in the crucible, and as silicon is only reduced by solid carbon, its reduction to silicon takes place at the same time as that of iron oxide to metallic iron. The silicon is dissolved in the iron, and by its presence causes the carbon to precipitate out as graphitic carbon, and there is thus obtained the soft grey iron desired. We are also of the opinion that in a furnace having a rectangular-shaped crucible, such as has the California furnace, the temperature of the charge in the crucible as a whole is much higher than is the case in a furnace of the Swedish type, and this higher temperature is more favorable to the reduction of silica to silicon, the latter, as before stated, being largely the controlling element in the production of soft grey foundry iron.

The Use of Calcined Limestone.—This has been repeatedly suggested, and theoretically it is the proper thing to do, but when operating a furnace of the Swedish type there are two objections to its use, namely:

1. It increases the percentage of fines in the charge.

2. It makes the charge hang.

As to the former of these objections, the idea seems to be more or less prevalent that there is no limit to the percentage of fines that may be used in the electric reduction furnace. We are not definitely informed in regard to this point with reference to the California practice, but judging from observations made upon the smelting of black sands, when the furnace consisted simply of a crucible and no shaft, more or less difficulty was experienced on account of the charge being made up entirely of fines. In the Swedish practice, the matter of the proportion of fines that can be used in a charge was definitely determined in the work at Trollhattän, and it was found that a large proportion of fines was detrimental to smooth running and good results, but Mr. Leffler, one of the engineers in charge of the work at Trollhattän, states that he is of the opinion that calcined limestone may be advantageously added to the charge if no reduction is attempted in the shaft.

Summarized, then, we may say that the California practice as compared to the Swedish practice presents the following advantages:

1. Permits the use of limestone calcined outside the furnace.

2. Does not require the circulation of gases.

As to this latter point, and also as to reduction in the shaft, we are not sure but what the California practice would prove more efficient if both were done. Although a very full and complete record of the working of the furnace at Trollhattän has been published, such is not the case as regards the operation of the furnace at Heroult, and so it will not be possible to make a definite comparison of the two practices until it is possible to receive as definite information in regard to the working of the furnace at Heroult as is now available in regard to the operation of the furnace at Trollhattän.

LINES ALONG WHICH THE ELECTRIC FURNACE WILL PROBABLY BE IMPROVED.

The Size of the Unit.—In Scandinavia the furnace has gradually been increased in size until now there are 3000-hp. furnaces in operation and A. B. Elektrometall have completed a design for a 7,500-kw. fur-

nace. Naturally the problem in connection with a furnace of the Swedish type is to get such an arrangement of the electrodes as to insure a practical uniform heating of the whole contents of the crucible, and at the same time maintain the elctrical equilibrium of the power system.

It is quite certain that the Swedish type of furnace will be improved along this line, namely, increase in size of the unit, and it is for this reason that results obtained from the operation of a furnace designed for 7,500 kw. will be awaited with great interest.

As for the California type of furnace, it will no doubt the possible to indefinitely increase the length of the same, just as has been done with the modern rectangular copper blast furnaces.

EFFICIENCY.

The efficiency of the furnace will also be increased as time goes on, and probably by improvements along the following lines:

(a) The utilization of the waste gases.

(b) The securing of a high power-factor.

(c) The correction of induction losses.

(d) The further study of the single-phase furnace vs. the three-phase furnace.

As regards the latter, inasmuch as practically all large power installations are three-phase, it would seem that the only logical thing to do is to use three-phase current in electric furnace work, but from data submitted by Catania it would seem as if the mono-phase furnace is more efficient than the poly-phase furnace.

SUMMARY.

Summarized then, we may say that the electric iron reduction furnace has passed the experimental stage; that it is meeting the requirements in those localities where it has been introduced, and that it will no doubt find extended application in those countries where the conditions are favorable to its introduction, namely, where electric power is comparatively cheap and where coke and charcoal are comparatively high. Inasmuch as the cost of electric power is largely the governing factor in determining its adoption, and as the cost of electric power is constantly decreasing, we may expect to find an extended application of the electric reduction furnace in the future.

The U. S. Consul at Leed, England, reports that what is said to be a successful synthetic tannin has been discovered by Dr. Edmund Stiasny, assistant professor of the leather industries laboratories of the University of Leeds. The new tannin, which is called Neradol, is made from tar distillation products, the synthesis being carried out by sulphonating cresylic acid and combining it then with formaldehyde. The white color of the Neradol-tanned leather and the brightening and bleaching effect of Neradol when used in combination with other tannins (vegetable and chrome) are especially noteworthy.

COMPOSITION OF CHINESE PAPERS.

M. Vidal, writing in *La Cellulose,* states that the papers used in China may be divided into two groups; those that contain only the raw materials of the far East and which we can regard as indigenous or almost so, and those made from the same materials that are used in Europe.

The first named are naturally the most interesting. Among them we find bamboo, broussonetia (*B. papyrifera*), edgeworthia and rice. He does not mention ramie, which he has not met with. Bamboo prevails and to a great extent. In all the samples containing it, it had been employed alone, without admixture. It is made into writing papers, very light and as a rule somewhat creamy, but nevertheless difficult of identification at first glance, in spite of the uniformity of their composition. Among the most remarkable he mentioned the account books of a merchant, fancy note and commercial papers, and also a certain blotting paper, sold as such and really blotting very well, though very thin, silky and almost glossy.

With the broussonetia or paper mulberry, either along or mixed, curious crimped papers are manufactured and gauzes, resembling fabrics and which serve also almost the same purposes in fans, handkerchiefs, tea table cloths, etc. From broussonetia are also made thicker papers, of astonishing indestructibility which are used as covers for school copybooks, pamphlets, etc., and also for wrapping expensive goods like silks.

Edgeworthia or *Mitsumata japonais,* enters into the composition of very beautiful papers, resembling mother-of-pearl. Used pure, it constitutes the real "imperial paper" of Japan. Mention was made of a magnificent, thick, white paper, and a pretty peel paper of wonderful fineness and flexibility.

He found rice paper but once. It was mixed with broussonetia and edgeworthia in a muslin paper. This straw is evidently not strong enough to be used in the thin papers that the Chinese prefer.

Finally, he said, we must not confound with rice straw, the false Chinese "rice" paper. This, as is well known, is not a paper, nor is it made with rice, but it is composed of fine slices cut off the pith of an aralia. This curiosity, formerly more common in France, continues to be used in the preparation of miniatures, pictures in water color or aquarelle, with which the ladies like to decorate their apartments.

The European products are mainly intended for printing papers, but not exclusively. Without being complete, the encroachment already includes a few of all sorts from the most delicate papers to the coarsest wappings.

Consequently, therefore, if we study papers originating in the middle kingdom, in the hope of finding rare fibers, we may meet with frequent deceptions; pine, very much pine, alfa, ordinary straw—these are

the varieties that may be found in the precious sample, so long coveted.

The large newspapers, the postal cards, the letter papers, etc., are of European origin and imported through the ports of Canton and Shanghai. They all contain more or less mechanical pulp, wood and alfa cellulose and rags.

On the other hand, there are established every day in China itself, especially in the province of Hankow, mills on the European plan. The earliest were established by foreigners, chiefly by the English, but they are passing more and more into the hands of the natives. It is possible that in the near future, they may render the importation of European goods unnecessary.

Thus the Chinese, our teachers, imitate us in turn. It is a long time since the two famous Chinese prisoners of war at Samarkand, revealed to us the secret of the manufacture of paper, and now we ourselves have found out something very important; that is the industry of cheap papermaking.

It is this industry, low priced paper, which has given birth to those two Siamese sisters, those unseparably joined twins, that we know as the press and advertising. And we know the tremendous success, not always of the highest standard unfortunately, that has attended them. It is this monster, well worthy of the infernal imagination of the "western devils," which after having turned Europe upside down, has dragged from the lethargy of sleep, China, that old China, which we believed to be unchangeably set in its ancient methods.

Probably some day, when the world uniformly knows only paper made from wood, when rags, valuable and rare, shall be reserved only for bank notes, there will still be, at the end of the remote provinces, some very ancient mills, which by thousand year old processes, using indigenous fibers long since abandoned, continue to turn out, after the fashion of some amateurs, artistic and ancient letter papers, ornamented, according to antique styles with flowers, insincere passages and formulas of politeness, printed in archaic characters.

The stock of turpentine on hand in Hamburg, the principal importing center of Germany, on Jan. 1, 1913, was double that of the previous year. The price of turpentine in Hamburg on that date was 6.9 to 7 cts. per pound, and had declined 6.5 cts. per pound on March 19. Fairly normal conditions are said to prevail. The price of resin on Jan. 1 was 2.9 cts. per pound, and on March 19 had dropped to 2.5 cts. per pound, tare 14 per cent. Prices have reached 3.3 cts. per pound since Jan. 31.

In 1912 Russia produced 36,868 short tons of copper, as against 28,294 tons in 1911. This output did not cover the requirements and about 8,280 tons were imported.

CONDITION OF THE ALUMINUM INDUSTRY.*

The aluminum industry has been brought before the public eye during the past year to a greater extent than hitherto owing to the fact that the Aluminum Company of America has been the object of investigation by the Department of Justice. The metal industry, along with the other friends of this company, has been gratified to note that this investigation failed to reveal any abuse of the monopoly of the manufacture of aluminum enjoyed by the Aluminum Company of America in the United States. It is reported that competition is about to arise, however, in the Southern Aluminum Company, which is engaged in preparations to manufacture aluminum with electric power secured from the Yadkin river at Whitney, North Carolina. The projected size of this new aluminum company and the fact that the importation of foreign aluminum is being stimulated by a keen demand assures to the aluminum consumers of the United States a sufficient source of supply of the metal to remove any possible embarrassment which might arise due to dependence upon a single source of supply.

During the latter part of 1912 the aluminum market was brisk, as was true of all other metals, and the demand has recently exceeded the supply not only in the States but equally so in Europe. The inconvenience to consumers which would naturally arise under such a condition has been considerably hastened and augmented by the metal brokers here and abroad who have contracted ahead during the past year for large quantities of aluminum for the purpose of doling it out at prices considerably in advance of those at which they purchased. A general slackening in the trade during December, however, will discourage speculation of this sort and encourage those who are in touch with the situation to believe that the embarrassment which the consumers have lately experienced will not continue during the year 1913.

The Aluminum Company of America has been endeavoring for some time past to increase its production capacity, but has been confronted with difficulties in securing adequate source of supply of electric power. Most of the water power developments which are sufficiently large to meet the requirements of this company are subject to some sort of governmental control, and the Government seems inclined to misinterpret the commendable policy of reasonable conservation into one of entire prohibition of development of any sort, a practice that might not improperly be characterized as miserly and one which certainly is working a hardship on the entire electro-chemical industry of the country and on all whose needs are served by this rapidly growing industry. The Aluminum Company has been fortunate, however, in securing the certain riparian rights located in North Carolina and Tennessee. Its plants contemplate the development of this water power on the most economical basis for

*From The Metal Industry.

use in a large aluminum plant to be constructed at once at such nearby point as will afford good freight rates and labor market. Until its own power development is completed the company will use power supplied by the Tennessee Power Company from their development on the Ocoee river near Chattanooga, Tennessee. This new aluminum plant will be in operation by the middle or latter part of the present year.

In addition to its extensions in the South the Aluminum Company is working on an extension to its Massena, New York, plant which, when completed in 1914, will give that plant the distinction of being the largest aluminum production works in the world. It is also stated that a large supply of electricity will be brought to Massena from the development on the St. Lawrence at Cedar Rapids. A part of this extension will be in operation in 1913 and the entire extension will be completed in 1914.

An entirely new branch of the industry in which the Aluminum Company has lately embarked is the manufacture of powdered aluminum known to the trade as aluminum bronze powder and employed widely as a paint pigment, in explosives and also in lithographing and printing. The experimental plant located at Dover, New Jersey, having proved quite successful, has been moved to new quarters at New Kensington, Pa., where the company now has in operation one of the most complete aluminum bronze plants in the world.

Other enlargements have been made at the New Kensington works; notably the construction of a plant for the manufacture of tanks, cooking vats and similar vessels which, made of aluminum, are finding high favor among brewers, preserve manufacturers and all industries where its heat-conducting, non-corrosive and non-poisonous qualities recommend aluminum. A considerable extension has been made to the cooking utensil factory located at this point, and a thoroughly modern boiler house is also being installed. In line with the usual progressive policy of the Aluminum Company of America, the company also plans a construction of an elaborate building for the convenience and comfort of its employes, in which will be a lunch room, bathing facilities and numerous other conveniences.

The most notable growth in the aluminum industry during the past year has been in extruded forms, tubing and aluminum foil. The many difficulties which attended the early efforts at extrusion have practically all been mastered and it is now possible to supply extruded aluminum of high tensile strength and very compact structure in practically any form desired. The use of aluminum tubing has also been growing, so much so, in fact, that the Aluminum Company is planning a considerable extension to its tubing plant at New Kensington.

The manufacture of aluminum foil is not a new application of aluminum by any means, but this use has always been limited owing to the high cost of the foil. Improved methods, however, have permitted a considerable reduction in price of aluminum foil and its use is now being pushed in several lines from which it was hitherto barred by its high cost. It is being largely employed in the manufacture of electrical condensers and for wrapping tobacco, candy and various food products where heretofore tin foil has been used. The Aluminum Company of America already has under way the construction of the largest aluminum foil factory in the world.

The Aluminum Company of America has been the world's pioneer in the manufacture of electrical conductors and in harmony with its forehandedness in this respect is now recommending an aluminum cable, steel reinforced, which consists of a seven-stranded cable—the six outer strands being of aluminum and the centre strand being of a steel of very high strength. It is claimed for this conductor that it possesses the highest qualities for transmitting electric current, and in addition has a strength which renders it particularly suitable in tower construction which is now almost entirely replacing pole construction of transmission lines. The Pacific Light & Power Company of Los Angeles, Calif., have adopted this cable for their new transmission line which is to be the longest in the world. It will carry electric power into Los Angeles from a power station located 275 miles distant. The Pacific Light & Power Company adopted this new aluminum cable, steel reinforced, only after having investigated all other conductors very carefully.

The U. S. Consul at Vancouver, B. C., states that it is reported that an extensive bed of rock salt has been discovered at Kwinitsa, on the Skeena River, about 45 miles from Prince Rupert, along the line of the Grand Trunk Pacific Railway. It has been known for some time that a deposit of salt existed at this place, and prospecting has been carried on with the result that a solid salt bed was struck by the drilling party. So far five holes have been drilled, in some instances over a mile apart, and in every case salt has been struck at depths varying from 50 to 250 ft. Up to the present about 8 tons of salt have been secured from the deposits. The discoverers have erected a small testing plant on the property, and the tests show that the product is absolutely pure and of the best quality. Owing to the long rail haul from eastern Canada a large percentage of the salt used in British Columbia is imported from California; consequently, should this find be as extensive as reported, it will be of great value to the Province, as large quantities of salt are used in connection with the fishing industry on this coast.

Wolfram exported from Federated Malay States in January, 1913, weighed 54,267 lbs., which Consul General Cunningham says was 28,000 lbs. more than in January, 1912.

WATER IN PAPERMAKING.*

By CHURCHILL HUNGERFORD

Depending largely upon the character of paper made and the stock used, the quantity of water required to manufacture a pound of paper ranges from 160 to 400 lbs. The fiber from which the paper is made is intimately associated with water from the time the stock is washed until the final product has passed over the driers. As the various processes of washing, boiling, beating and refining are all conducted in the presence of enormous volumes of water it is apparent that even a small proportion of impurities in that water would amount in the aggregate to large quantities. For instance, assuming that a 20-ton paper mill uses 1,200,000 gals. of water in a day, and that this water contains three grains of suspended matter to the gallon—a rather small content for most natural waters we find that in the manufacture of that twenty tons of paper we have introduced extraneous matter in excess of 500 lbs. This is equivalent to 25 lbs. to the ton. No sane person would think of shoveling into every ton of paper stock an indiscriminate mass composed of decayed leaves, bark, sand, red clay, iron, etc., and yet he might be totally oblivious to the fact that his water supply is carrying in twice this quantity of deleterious matter.

Perhaps the character of the impurities in the water is of greater importance than the quantity. It is conceivable that certain forms of contamination might exist in considerable quantities without making serious trouble, while other substances, such, for instance, as iron oxide in very small quantities, might prohibit the use of the water. This is frequently seen in water from wells which is perfectly clear when first pumped but which afterwards shows a slight deposit of iron. There may not be more than an eighth of a grain of iron to the gallon and yet it may cause discoloration of the fiber. On the other hand, the water might contain a large amount of lime or magnesium, perhaps ten or even fifteen grains to the gallon, and yet be quite suitable for papermaking.

The obvious remedy for all water troubles is filtration. It seem to be the consensus among papermakers that so far as the effect on the fiber or the quality of the paper turned out is concerned the product is not particularly influenced by the presence or absence of hardness in the water. Theer does not seem to be any particular reason why it should be influenced as most of the fibers used in papermaking have no tendency to absorb the lime salts. This means that water-softening—a somewhat troublesome and complicated process at times—need not be resorted to for any other purpose than the treatment of the boiler water.

A seriously neglected phase of water purification among those manufacturers who have already installed filters is the absence of a chemical treatment in conjunction with the straining process of the filters. It is quite apparent to anyone that dissolved matter will pass through any filter. It is also equally apparent that if dissolved matter is reduced from a liquid to a solid form of not too fine a grain it can be retained by any good filter. Now, many of the most troublesome impurities present in water are either in a fluid or semi-fluid form or so finely divided as to be equivalent to fluids, so that they cannot be adequately retained by the filter without chemical treatment.

Foremost among the impurities requiring chemical treatment is the so-called vegetable matter that gives the waters of the New England States and other localities a dark color. This stain is due largely to natural dyes extracted from decomposing leaves and from cedar, laurel and peat swamps. These are really quite effective dyes, especially when brought into contact with the cellulose fiber after the customary boiling in the digesters, which removes the natural protective coating. These natural dyes have a tendency to color strongly such cellulose, but a more important factor and one that greatly increases their coloring power is the use in papermaking of strong coagulants for various purposes which precipitate these colors and mordant them on to the fiber. The most noteworthy of these coagulants is the alum which is used in precipitating the size and in mordanting many of the colors with which the paper is dyed. Other mordants besides alum are also used in dyeing and nearly all react strongly upon the coloring matter existing in the water.

To illustrate both of the above statements it is necessary to consider the process to which the fabrics which eventually become rags were subjected. The fabrics, after being woven, were sent to a bleachery where they were first boiled with caustic soda in large pressure tanks called kiers. These kiers are quite similar to digesters. After a certain time the gums, resins, fats, etc., which acted as a protective coating for the fiber, were dissolved, leaving the fiber pure cellulose. Before boiling, the fabric could not have been bleached. After boiling it could be readily bleached by the same process used in the paper mill for bleaching paper stock, and in addition was made extremely sensitive to many dyes. This fiber again goes through practically the same treatment when it falls into the papermaker's hands and is rendered if possible even more sensitive to dyes than before. When this stock is broken up in the beaters and the water mixed thoroughly through it, all of the coloring matter comes into intimate association with the fiber and is entirely absorbed, changing the color somewhat. The coagulants used set or mordant this color so that it remains permanently in the fiber and cannot be removed by the ordinary processes of washing. As a result the much desired brilliant white is toned to a cream or an ivory tint of greater or less intensity.

The quantity of deleterious matter that is precipi-

*From Paper.

tated from the water in the manufacture of paper can be readily demonstrated by an interesting experiment which will probably surprise very many paper manufacturers, both those who have filters and those who have not. This experiment consists in the filling of the large, clear glass or bottle with water from the stream and adding some alum or sulphate of aluminum to it, stirring it for several minutes to insure a thorough mixture, and then allowing the water to settle for an hour or two. Before the alum is applied the water may be clear, practically colorless as viewed in the glass, and free from suspended matter. Half an hour after the addition of the alum the water becomes somewhat turbid and flocculent matter will be visible all through it, some precipitated matter coming to the surface and some settling to the bottom. A portion of this matter is the decomposed alum that has been applied, but most of it represents what is generally called vegetable matter and whatever suspended inorganic matter may have been present in the water. It all has a marked affinity for cellulose and will attach itself to it if placed in contact with it.

This same process is duplicated in the beaters when alum is applied for the precipitation of size or for mordanting the colors. Not only is the size precipitated but this coloring matter made visible in the experiment is precipitated also and a very decided change in color of the paper is sometimes effected. Filtration without a coagulant does not prevent discoloration because the color is in solution and readily goes through the filter, only to be deposited on the fiber later. If this coloring matter contains a little iron—and it frequently does— the color of the paper will change very materially with age. As to the mordanting of the dyes, while alum is not the only mordant used any of the other mordants will produce the same effect of coagulating the vegetable matter, and it frequently happens that a color that will develop a pink at one stage of the river will develop a salmon color at another, merely for the reason that the yellow existing in the water at low stages of the stream is precipitated on the fiber as well as the pink dye, and the color is changed.

The only and certain way to keep the alum and other coagulating substances used in paper manufacture from precipitating the foreign matter on the stock and causing the above undesired results, is to anticipate the process of coagulation in the filter plant itself and to apply a coagulant in sufficient quantities to precipitate all of this foreign matter before the water itself is passed through the filter. Having given the water this treatment and afterward passing it through the filter it will be impossible to produce any further undesired precipitation from the fact that all of the offensive matter has been precipitated and retained in the filter.

It is quite evident that the small particles of matter floating in water will make specks in the paper. Although comparatively small they seem to possess the power of flattening out under the calender rolls to make very large specks. Filtration, of course, removes these particles, but filtration with proper chemical treatment goes further; it gives a water that can produce a prefectly white sheet of paper, free from any water-borne discolorations.

Few paper mills in the present day are so fortunately located as to have their water supply free from contamination by industrial wastes. It may be that the waste comes from other paper mills, from textile mills which use large quantities of dyes, soaps, etc., or that sewage is emptied into the stream. A paper mill is not a plant that can be picked up and moved about readily, and all the good sites were long ago preempted, so that many of the papermakers of the more thickly populated part of the country have seen, during the past ten years, their once good supplies converted into water of the most dubious aspect. The saving grace of this situation is that the art of filtration has advanced a little faster than the streams have deteriorated, with the result that the filter man can in almost every case suggest a plan of preliminary treatment and filtration that will make a highly polluted water better for paper making than it was before contamination.

All purification plants are not by any means alike but are designed to meet the condition that exists at the place of installation. The filter man studies the situation, makes a note of the various forms of contamination, their quantity, their proportion with regard to the normal flow of the stream, and then submits a plan for a plant that he knows will meet the situation. For badly polluted waters the plant consists of a settling basin for the preliminary treatment of the water with chemicals and of a filter plant for removing whatever precipitated impurities have not settled to the bottom.

Generally speaking all the chemical treatment that is required is the addition of alum. The alum as already stated precipitates the natural colors that exist in the water and it also precipitates nearly all of the artificial dyes. It also coagulates any soap that may be in the water, precipitates the sewage, and gathers together various nondescript particles of matter which have the same specific gravity as the water and would not otherwise settle. The action of the alum is very rapid indeed, so that in a short time after the addition of this coagulant the flocculent matter is quite visible to the naked eye. When flocculation takes place sedimentation follows with great rapidity, so that two hours' sedimentation with alum will often produce a greater degree of clarification than two days' sedimentation without it.

The alum is applied to the water as it enters the sedimentation tank and in this tank baffles are so arranged that the water takes a circuitous course. If this were not done the water would take a direct line from inlet to outlet and instead of remaining for a period of several hours within the basin it would pass

directly across it in a few minutes and the necessary chemical action and sedimentation would not be completed. For waters not badly polluted the settling tank is very frequently omitted, the alum being applied as the water enters the filter, sufficient chemical action taking place to precipitate the impurities.

In some cases the water is so soft that the alum is not effective. This is because the alum requires an alkali to decompose it and it is in the process of decomposition that all of the beneficial results desired are obtained. The deficiency in alkalinity is made up by means of small quantities of lime or soda, which are applied to the water, and the alum, having the alkali to decompose it, operates actively and produces a profuse precipitate.

This action of alum can best be explained by describing just what alum is. The active agent in alum is sulphate of aluminum, which is made by combining sulphuric acid and clay. When the sulphate of aluminum is dissolved and applied to a water containing carbonates of lime and magnesia, both of which are strong alkalies, the sulphuric acid, having a greater affinity for the strong alkali of the lime and magnesia than it has for the weak alkali of the clay, leaves the alum to combine with the lime and the alum goes back to what is virtually an insoluble clay called hydrate of alumina. The hydrate formed by the decomposition of the alum when perfectly fresh is quite gelatinous and sticky and it is this gelatinous property which causes it to gather together all of the particles of matter in the water.

In a few extreme instances the streams show pollution to such a degree that the matter precipitated by the alum is not only redissolved by bacterial action in the sludge at the bottom of the chamber, thus liberating much of the precipitated matter, but large quantities of gas are generated which tend to buoy the sludge to the surface, nullifying the objects aimed at in the settling basin. Where this condition is encountered—and fortunately such cases are rare—antiseptic treatment of the water must be resorted to and hypochlorite of lime, or, as it is more familiarly known, chemical or bleaching powder, is the agent which entirely arrests this process of fermentation. Usually from sixteen to twenty-four pounds of bleaching powder per million gallons of water will entirely stop the process of fermentation, and the alum, if properly applied, will then perform its full duty and cause the settling basin to remove a very large proportion of the suspended matter.

Of the alum and hypochlorite of lime used, no trace of either, as such, remains in the filtered water when the chemical feeds are correctly adjusted. The alum is decomposed into its original elements and is filtered out, and the hypochlorite of lime (calcium hypochlorite) is changed into a substance very similar to common table salt. In fact, it forms quite a considerable proportion of the impure sea salt occasionally encountered.

It is always an advantage to utilize a sedimentation basin wherever it can be done, because it retains much of the heavier impurities, leaving the lighter matter to be retained by the filter. This is an ideal condition. While a filter is able to handle very bad water without any preliminary sedimentation, its true function is more of a finishing process, and it is a mistake to use it to handle water containing much suspended matter. However, a great many waters, particularly those of the New England section, are not seriously contaminated, and the pressure type of filter without sedimentation can be very economically used. With this type of installation the water is usually pumped from the stream through the filter and on to the various points at which it is used, all in one process, the filters reducing the pressure from two pounds to ten or fifteen pounds, depending upon the make. The alum is applied just as the water enters the filter, produces the desired results, and is filtered out.

Under the above conditions, the pressure filter gives quite as satisfactory results as the gravity filter, and in many instances possesses a certain superiority. One particular advantage of the pressure filter lies in the fact that by its use double pumping can frequently be avoided.

There exists, even at the present time, an unfair prejudice against pressure filters, from the fact that in the past many of them were very carelessly constructed and the manufacturer who was unfortunate enough to possess such a filter and afterwards purchased a gravity filter plant reached the conclusion that the gravity system is superior to the pressure, when, as a matter of fact, he is really comparing a well-constructed filter with one that was poorly constructed. Fortunately, many filter manufacturers of the present day have brought their pressure filters up to the same efficiency as their gravity filters.

As so much space has been devoted to the advantages derived from chemical treatment of the water, it is not inopportune to give a description of the manner in which the chemicals are applied.

For reasons of economy, it is desirable to apply the least amount of coagulant that will do the work. At the same time, it is necessary to employ enough chemical so that complete coagulation of the objectionable matter may take place. The great problem in filtration is to meet the ever-varying changes in the rate of flow of water through the purifying plant. This rate of flow may fluctuate from 50 to 75 per cent in a few minutes, and if the chemical feeds do not instantly adjust the amount of chemicals to meet these fluctuations in flow, we have an excess or a deficiency of chemical. A deficiency means poor water and an excess may mean dangerous water, particularly where the paper is being dyed. The properly designed chemical feed meets these fluctuations perfectly. As most of these devices are patented, it would not be opportune to go into a lengthy description of them, but the

prospective purchaser should satisfy himself thoroughly that he is getting a chemical feed which can apply with certainty the proper amount of coagulant at all times. The amount of alum or sulphate of alumina required ranges from ¼ grain to 2½ grains per gallon. This would make the cost of coagulants range from $1 to $4 per million gallons.

As to the filter, whether it is of the gravity or the pressure type, a few vitally important facts are to be considered. First, will the filter deliver crystal clear water at all times? Second, will the filter wash so thoroughly that there will be no requirement for renewal of the filter bed or removal from the case for additional washing? Third, is the strainer system—the vital part of the filter which collects the filtered water and distributes the wash water—so designed and of such a character that it cannot become obstructed and thereby cause incomplete washing of the filter bed? Again, is the filter so designed that it will wash thoroughly in from three to five minutes?

The manufacturer who has a filter that does not deteriorate, that never requires a renewal of the filter bed, that requires only a few minutes' attention daily —and that only from an ordinarily intelligent laborer —and, above all, that holds surely and certainly all of the accumulated matter within its depths when filtering and gets rid of it rapidly and completely when washing, has the type of filter that will make a paper plant successful. There are such filters, but unfortunately there are still a great many paper mills in the country that are using makeshifts which are taking a yearly toll from their profits.

The U. S. Civil Service Commission, Washington, D. C., from whom further information can be obtained, announces an open competitive examination for laboratory assistant in ceramics, for men only, on June 4, 1913. From the register of eligibles resulting from this examination certification will be made to fill several vacancies in this position in the Bureau of Standards, Department of Commerce, at salaries ranging from $900 to $1,200 per annum, and vacancies as they may occur in other branches of the service requiring similar qualifications, unless it is found to be in the interest of the service to fill any vacancy by reinstatement, transfer, or promotion. The person or persons appointed to this position will be stationed at the Pittsburgh, Pa., laboratory of the Bureau of Standards, and will assist in original investigations in the chemistry and physics of clay and clay products. An educational training equivalent to at least four years of collegiate work in a technical school, which must include not less than one year's training in ceramics, is a prerequisite for consideration for this position.

Cider making and cheddar cheese chemistry investigations have been inaugurated by the University of Bristol, England, under special grants.

ALUMINIUM NITRIDE.*

By J. W. RICHARDS.

INTRODUCTION.

The production of aluminium nitride (AlN) on a large scale is proposed in the electric furnace process of Ottokar Serpek, followed by the decomposition of the same by water or caustic soda solution, thereby liberating the nitrogen as ammonia and producing alkaline aluminate solution from which pure alumina can be obtained. This rather daring chemical proposition has directed attention to aluminium nitride, the conditions of its formation and its properties.

The existence of aluminium nitride was suspected for some time before it was isolated. A rather indefinite number of years ago, probably about 1890, the attention of the writer was directed by his father to the fact that when metallic aluminium in a melted condition was skimmed, and the skimmings or dross laid to one side, that on pouring water upon them, while still warm, these skimmings gave off an odor of ammonia. The explanation which was then figured out for this phenomenon was that the hot aluminium in the skimmings oxidized to alumina, and that the rather high temperature thus produced locally caused the aluminium to unite also with the nitrogen of the air and form nitride. In other words, that some of the aluminium united first with the oxygen and immediately thereafter some also with the nitrogen of the air. On sprinkling with water the nitride would react according to the following equation:

$$2AlN + 3H_2O = Al_2O_3 + 2NH_3$$

In the light of subsequent investigation and the formation of aluminium nitride in other ways, it appears that the explanation given in these early days was correct and that aluminium nitride is formed directly under such conditions from metallic aluminium and the nitrogen of the air.

Le Verrier, later, proved the presence of traces of nitrogen in commercial aluminium by dissolving it in caustic potash and passing the nitrogen evolved into Nessler solution, obtaining from it the ammonia reaction. He thus proved the presence of nitrogen in the metal and suspected it to occur as aluminium nitride dissolved in the excess of metal. In further experiments he treated aluminium with a current of nitrogen gas until it was saturated, and noted that this produced considerable diminution in the tensile strength, elastic limit and elongation of the metal.

Prof. Mallet later obtained aluminium nitride corresponding closely to the formula AlN by heating metallic aluminium in a carbon crucible to a moderate temperature for several hours, in contact with dry sodium carbonate. Some alumina is formed, some

*Paper read before the New York Section of the American Electrochemical Society, Feb. 7, 1913, and called up for discussion at the 23rd General Meeting of the American Electrochemical Society, at Atlantic City, N. J., April 3-5, 1913.

sodium vaporizes and some carbon is deposited; the reaction is probably as follows:

$$3Al + Na_2CO_3 + N = AlN + Al_2O_3 + C + 2Na$$

Aluminium nitride containing 34 per cent of nitrogen and 66 per cent of aluminium was obtained as little yellow crystals and amorphous drops. When calcined in the air it was found to lose nitrogen and form alumina; it was decomposed in moist air, losing its transparency, becoming lighter yellow, evolving ammonia gas, and finally leaving the alumina residue. Caustic potash solution and melted caustic potash both attacked it actively, disengaging ammonia and forming potassium aluminate.

A later experimenter described the compound as a gray amorphous powder, but with properties otherwise similar to those described.

THE SERPEK METHOD.

Coming now to the work of Serpek we find his first proposition to be the production of aluminium nitride from aluminium carbide, which is indeed a possible reaction. In his U. S. patent 867,615 (filed June 19, 1906, issued October 8, 1907), he describes the passing of nitrogen or a gas containing nitrogen over aluminium carbide as an initial material heated to red heat. He describes the volume of the carbide increasing as it is converted into nitride, and that the absorption of nitrogen was increased by diluting the carbide with such materials as carbon or aluminium chloride; also that traces of hydrochloric acid or sulphur dioxide in the gas currents facilitated the conversion. The claims of this patent are essentially for the method of producing aluminium nitrides by heating aluminium carbide in an atmosphere containing nitrogen to a red heat with or without the diluting substances admixed and with or without traces of acid gas in the nitrogen used.

Attention may be called to the term "aluminium nitride" in this patent, corresponding to the fact that in the product thus obtained by Serpek he found that part of the nitrogen in the product was driven off by contact with air, and a further part by boiling with water, and a still further part by treatment with caustic alkali solutions. These facts pointed to the non-homogeneity of the product, which thus appeared to consist of a mixture of different nitrides instead of one distinctive chemical compound.

Continuing his work, we find that Serpek later concluded that it might be possible to obtain the nitride directly from mixtures of alumina and carbon, which it will be recalled he used as diluent substances in the conversion of the carbide. He was apparently not able at that time to produce nitride directly from these two substances, but found that in the presence of a small amount of a metal, such as copper or iron which is capable of forming an alloy with aluminium the formation of nitride from the mixture took place. In his U. S. patent 888,044 (filed May 24, 1907, issued May 19, 1908), he describes mixing alumina with carbon in the proportions necessary for formation of CO gas ($Al_2O_3 + 3C$), adding about 5 per cent of either copper or iron or a mixture of the two, and heating the mixture to a red heat in a current of nitrogen gas, at which temperature the partial formation of an alloy of aluminium, produced by reduction, with the copper or iron would be initiated. The idea seems to have been to produce a mixture on the point of reaction from its constituents and then to super-add the influence of the current of nitrogen gas. Traces of HCl or SO_2 gases are said to facilitate this reaction also, and the product is described as almost pure aluminium nitride. The reaction is described as developing a high temperature as soon as it is initiated. The claims are for producing aluminium nitrides by heating the mixture of alumina with carbon and a metal capable of forming an alloy with aluminium, to red heat in an atmosphere containing nitrogen, with or without the presence of small amounts of acid gases.

It is evident that in this method the conversion of alumina into aluminium nitride was aimed at, with the assistance of small amounts of metals as catalytic or assisting agents. Whatever may have been the results of this process, it led the investigator in the end to the method described in Serpek U. S. patent 987,408 (filed December 15, 1909, issued March 21, 1911) in which aluminium nitride is produced directly from Al_2O_3 and carbon in the presence of nitrogen, at a much higher temperature than previously recommended. This patent appears to be the result of considerable investigation on the conditions of this direct production, and specifies very exactly the temperatures at which the direct conversion takes place. The patentee speaks of the general supposition that extremely high temperatures would be required for such direct conversion, such as the highest temperatures of the electric furnace, but explains that by careful investigation he had found that if the temperature is closely watched some combination of nitrogen with aluminium can be observed even at 1,100° C.; that at 1,500° nitrogen is absorbed fairly rapidly, at 1,700° energetically, and that at 1,800 to 1,850° the reaction may be almost designated as violent, producing almost chemically pure nitride. Further, Serpek found that temperatures higher than this gave a smaller yield, and that somewhere above 2,000° the production practically ceased, the decomposition temperature of the nitride appearing to be about 2,120° C. This brilliant piece of experimental work really laid the foundation for the Serpek process as it now exists. The inventor further discovered that impure alumina, such as bauxite ore, was converted at somewhat lower temperatures than the pure material, evidently owing to the catalytic effect of the impurities present.

The claims of this patent are for producing aluminium nitride by heating aluminous compounds and carbon, or more specifically alumina and carbon, in an atmosphere containing nitrogen to temperatures not exceeding 2,000° C., and preferably about 1,800°.

Reference may very properly be made at this point to the experimental investigations and confirmations

of these results by Prof. S. A. Tucker and Henry L. Read, given before the Eighth International Congress of Applied Chemistry, published in its Transactions, and in volume XXII, of the Transactions of the American Electrochemical Society. This investigation, carried on in the electrochemical laboratory of Columbia University under carefully regulated conditions, showed traces of nitrogen absorbed at temperatures of 1,000 to 1,100° and as much as 30 per cent of nitrogen in selected portions of the product made between 1,800 and 1,900°. The product made at higher temperatures contained less nitrogen and was either sintered or fused. Impure alumina, such as bauxite, was found to be converted more easily than pure alumina, and the definite statements of the last Serpek patent were confirmed and verified.

THE SERPEK REACTION.

The decomposition of alumina by carbon in presence of nitrogen to form aluminium nitride is a reaction which is interesting to study and compare with analogous reactions.

Professor Baron, in 1760, tried to reduce alumina by carbon, but was unable to obtain the temperature required.

Oerstedt, in 1817, devised a way to decompose alumina by carbon, finding that this took place in a stream of chlorine gas, at a low temperature, the products being aluminium chloride and carbon monoxide gas.

$$Al_2O_3 + 3C + 3Cl_2 = 2AlCl_3 + 3CO.$$

This reaction is practically the exact analogue of the Serpek reaction, using chlorine instead of nitrogen. Deville, for instance, who ran this operation on a large scale, remarks that the retort is heated to a uniform dark-red heat (which would be about 600°C.) and that "however fast the chlorine may pass into the retort, it is so well absorbed during three-fourths of the operation that not a trace is mixed with the carbon monoxide escaping." If the query be made as to why the reaction is so easy, thermo-chemistry gives us the answer: the reaction is exothermic 17,880 calories.

$$Al_2O_3 + 3C + 3Cl_2 = 2AlCl_3 + 3CO.$$
$$-391{,}600 \qquad + 322{,}000 + 87{,}480 = + 17{,}880$$

It is profitable to consider in this connection another analogous reaction.

$$Al_2O_3 + 3C + 3S = Al_2S_3 + 3CO.$$

This reaction does not take place at 1,200° C., and we find it would be endothermic (heat absorbing) 180,200 calories. However, the reaction with carbon and sulphur already combined as CS_2 does take place, readily, at 1,000° C., and this reaction is much less endothermic than with C and S separately:

$$Al_2O_3 + 3CS_2 = Al_2S_3 + 3COS$$
$$-391{,}600 + 87{,}000 + 124{,}400 + 111{,}090 = -69{,}110$$

Coming now to the nitrogen reaction, we have:

$$Al_2O_3 + 3C + N_2 = 2AlN + 3\,CO$$
$$-391{,}600 \qquad + 90{,}900 + 87{,}480 = -213{,}220$$

This is therefore a highly endothermic reaction, and corresponding with that we have the fact that it does not take place to an appreciable extent below 1,500° C. Aside from all thermal losses, we can say, therefore, that the reaction itself absorbs 213,220 calories = 248 kw. hours for 82 kg. of aluminium nitride formed; which equals 3,000 kw. hours = about ⅓ kw. year per ton of nitride. At least double this amount would be required in practice.

THE SERPEK APPARATUS.

Serpek's U. S. patent 996,032 (filed June 21, 1910, issued June 20, 1911) contains a detailed description

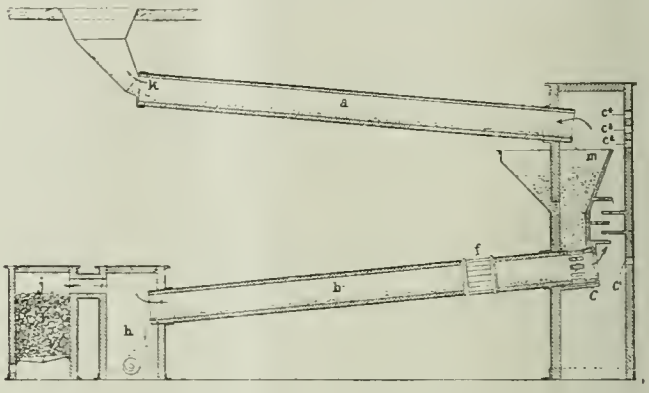


Diagram of Serpek Apparatus.

Serpek Apparatus: k, supply of ground bauxite and gas exit to chimney; a, calcining kiln; m, hopper in which calcined bauxite mixes with carbon; b, kiln for nitride reaction; f, electric resistance furnace; h, storage chamber for hot nitride; j, gas producer; c, chamber for deposition of fumes and dust; c^1 c^2 c^3 c^4, air inlet for combustion of gases from lower kiln. From Serpek U. S. Patent 996,032.

of apparatus intended for the commercial manufacture of the nitride from bauxite or other aluminium ores. The plant consists in two superposed rotating cylindrical kilns, similar in construction to a cement clinkering kiln. These kilns are inclined in opposite directions, so that the material being preheated in the upper kiln and passing from right to left, for instance, falls into the opening of the lower kiln for treatment at higher temperature where it passes from left to right. Bauxite alone is passed through the upper kiln, and there calcined; then mixed with the necessary carbon in its passage from the upper to the lower kiln, and the mixture treated by nitrogen at a high tempetature in the lower kiln, which is provided with a detachable electric resistance furnace about midway of this length and which is intended to subject the charge therein to the reacting temperature, about 1,800 to 1,900° C. The material is discharged from the lower end of this kiln into an air-tight receiver. A large gas producer of the ordinary type furnishes producer gas (approximately ⅓ CO, ⅔ nitrogen) to the lower end of the lower kiln. This gas entering at a temperature of about 400° becomes highly heated as it passes through the kiln in a direction contrary to the descend-charge, and at the electrically heated zone at a temperature of 1,800° to 1,900° reacts upon the mixture, forming nitride. After leaving the high temperature zone the gas enriched in CO coming from the reaction preheats the descending charge, issues from the upper

end of the kiln into a vertical closed chamber and passes through it to the opening of the upper kiln, where it meets a blast of air which burns it for the purpose of heating the contents of the upper or calcining kiln.

The apparatus as thus described achieves a methodical heating of the reacting mixture, utilizes the CO gas made in the producer and also that evolved by the reaction in the furnace; aims at an intimate mixture of the charge by the rotation of the cylinders and intimate contract of the nitrogen with the charge. The inventor states that the silica impurity of the charge is mostly volatilized (probably as reduced silicon) from the charge at the reacting temperature and is thus carried out in the gases; and that the apparatus may be used for producing other nitrides made by analogous reactions.

The claims cover an apparatus comprising the features of a revolving inclined upper cylinder discharging into an inclined lower cylinder revolving in the opposite direction, through a vertical chamber in which the gas from the lower cylinder may be burned, combined with a detachable electric resistance heating furnace within the lower cylinder. One claim is for the single features of a rotary calcining cylinder carrying a detachable electric resistance furnace.

Undoubtedly a large amount of excellent investigation has been put upon this process, and it certainly deserves commercial success. The method is being tested in France upon a large experimental scale.

A NEW FACTOR IN METAL FAILURES.*

By ERNEST A. LEWIS.

It has always been assumed that when copper, tin, zinc and lead are alloyed together by melting that only complicated chemical means could separate them. This is now known to be a delusion; they can be separated by physical means. Professor Turner in the course of his experiments on heating alloys in a vacuum found he could separate copper and tin from lead and zinc at a red heat. This is rather a difficult process, although it will very probably be worked commercially eventually. The Mond process of making nickel is a great success and the apparatus is far more complicated than the vacuum process would need. The writer has learned by experiment that in an atmosphere of hydrogen, zinc and lead can be separated from copper and tin at a red heat, considerably below the melting point, but not so well as in a vacuum. There is always 3 per cent or 4 per cent of zinc left in. The importance of this fact in the metal rolling business will be appreciated, when it is seen that hydrogen is a reducing gas. Further than this, in coal gas also, there is volatilization of zinc, but not so much as in hydrogen. Carbon dioxide is apparently an inert gas, as I have heated brass in a current of it and no volatilization takes place. It must be understood that there is very little chance of injuring copper by annealing in steam.

Many manufacturers have found remarkable red places on the surface of brass sheets after they have been annealed and pickled. Various suggestions as to the cause of this have been brought forward. An old suggestion was, that it was due to sulphur in the coal. Why this should be I do not know, as the iron pyrites in coal burns to sulphur dioxide and it is hardly possible this would affect the color; another suggestion and in some cases it is quite true, is, that it is due to iron in the pickling baths, but these peculiar marks come when there is no iron. They are quite different to the red tint obtained when brass and copper are pickled together. This bad practice is occasionally done. The probable cause of the red patches is that a reducing atmosphere has been formed in the annealing furnace, long enough to volatilize the zinc on the surface and leave the copper behind. Incidentally the experiments showed that although brass may contain traces of oxide it is not an essential constituent like it is of copper. In every case the turnings or sheet were perfectly soft and there was no sign of brittleness. Everyone who has heated copper in such a way as to reduce the oxide in it knows how brittle it becomes, because the oxide of copper is an essential constituent of practically all commercial coppers.

In locomotive types of boilers, which have brass tubes, it has often been noticed that the ends near the fire are corroded away. It is usually assumed that chloride in the coal is the cause of this, but it seems to me that it is far more complicated. A reducing atmosphere may be formed and this would favor volatilization of zinc and this, in conjunction with chlorides and sulphur, would cause rapid deterioration. The alteration of surface composition in yellow metal sheets for sheathing would favor corrosion in sea water. This alteration cannot be due to bad mixing of the metal at the time of manufacture, as has been suggested, but if the zinc can volatilize under certain conditions of manufacture, it would account for some cases of corrosion in patches.

The only satisfactory way to anneal brass is in furnaces where the flame does not touch it. It has been urged by manufacturers as an amelioration of the offense of pouring black smoke into the atmosphere, that it is necessary to anneal brass under such conditions. There is no necessity at all for such conditions; in fact, the reverse is the case, long "soakings" are found to be unnecessary.

*From The Metal Industry.

An English syndicate has acquired for $71,400 the patent rights for England and the colonies (not Canada) for the manufacture of yarns and cloth made of nettle fiber. The German company, with works in Schleswig-Holstein, will shortly begin actual working, and it is understood that they will specialize in the manufacture of yarns suitable for carpet manufacture.

METALLURGY.

UNIFORM NOMENCLATURE OF IRON AND STEEL.*

The Committee nominated for the solution of this problem is composed as follows:

Chairman of the Committee—Henry M. Howe, New York.

Vice-Chairman—L. Levy, Paris; D. Tchernoff, St. Petersburg.

Secretary of the Committee—Alb. Sauveur, Boston.

Members—Van Drunen, Ixelles; O. Busse, Copenhagen; H. Brauns, Dortmund; Verein Deutcher Eisenhüttenleute, Düsseldorf (Repr.: E. Schrödter); Jernkontoret, Stockholm (Repr.: I. A. Brinell, C. Benedicks, J. O. Roos af Hjelmsäter); F. W. Harbord, London; The Iron and Steel Institute (Repr.: J. E. Stead); L. P. Sidney, London; A. Pourcel, Paris; H. Le Chatelier, Paris; F. Osmond, Paris (†); Comité des Forges de France (Repr.: Saladin, G. Charpy); P. Verole, Milan; Associazione fragli Industriali Metallurgici Milano (Repr.: Ing. C. Vanzetti); A. Baalsrud, Christiania; A. R. v. Dormus, Vienna; A. Sailler, Vienna; Bureau des forges, St. Petersburg; N. Belelubsky, St. Petersburg; Service du contrôle et de la réception des commandes du Ministère des voies de comm. (Repr.: O. Klemm), St. Petersburg; Edvi Illés Aladár, Budapest; Lázár Zoltán, Budapest; Misángyi Vilmos, Budapest; W. Campbell, New York; Jos. W. Richards, South Bethlehem (Pa.); The American Society of Mechanical Engineers, New York; American Iron and Steel Institute (Repr.: Ch. Kirchoff, New York); American Institute of Mining Engineers (Repr.: Ch. Kirchoff, New York); Henry D. Hibbard, Plainfield; H. P. A., Tiemann, Pittsburgh.

INTRODUCTION.

With a few exceptions the definitions offered by your committee to the 6th Congress have been favorably accepted by the parties interested and we therefor recommend that they be accepted as standard. New definitions in place of those which seem to need amendment, and definitions of a few additional names, are proposed in this report.

Two names, "steel," and "malleable cast iron," need radical treatment in the opinion of part of this committee. Though colloquial and trade usage can easily tolerate two distinct and inconsistent meanings for a single name, scientific usage can tolerate them only reluctantly. Hence, some of us recommend taking steps to remove the inconsistencies connected with these two names.

A few additions and amendments to the glossary of our last report have been proposed, but these are so few that we do not burden the present report with a new glossary, and instead we propose to include a revised glossary in our next report, which we hope may be our final one.

Several eminent gentlemen identified with the industry have proposed including in the definitions a statement of the apparatus in which the several products are habitually made, for instance specifying that cast iron is made in the iron blast furnace. But any substance which is identical in nature with cast iron should the cast iron in scientific language no matter how it is made, whether by melting in a crucible, by cementation, by a stroke of lightning, or by any other means now unguessed. Such restrictions do not belong in a definition, the purpose of which is to set up metes and bounds, to part the thing defined from the rest of the universe. But in order to meet their wishes, we supplement the definitions proper with remarks, clearly not defining but cautionary in their nature, which explain how certain of these products are habitually made. Such an explanation may well be useful as an added safeguard against fraud, because an industrial contract presupposes that its own language is to be read in the light of existing industrial conditions and usage. That may be "cast iron" scientifically speaking which is clearly not "cast iron" industrially speaking, as a blind or moribund horse, though still a horse scientifically speaking, is clearly not a horse for most industrial and administrative purposes.

NEW DEFINITIONS PROPOSED TO THE SIXTH CONGRESS.

Official Definition.

Cast Iron.—Definition: Iron containing so much carbon that it is not usefully malleable at any temperature. In America, besides the foregoing generic meaning, "cast iron" is used also in a specific sense which excludes "pig iron" (see below) and is restricted to cast iron in the form of castings other than pigs and to remelted cast iron suitable for such castings.

Remarks: The cast iron of commerce is reduced from the ore, usually in the iron blast furnace, in direct contact with solid carbon, and is then tapped from the furnace in a molten state. It always contains an important percentage of carbon, usually from 2.5 to 4.5 per cent and in most cases an important percentage of silicon.

There are three chief varieties of cast iron.

Gray Cast Iron: Relatively soft, and characterized by the presence of sheetlets of graphite, often forming an irregular skeleton. This is the variety used chiefly for engineering work.

White Cast Iron: Extremely hard and brittle, characterized by having all or nearly all its carbon in the combined state, and by its consequent lack of graphite.

*Report of Committee 24, presented by H. M. Howe, Chairman, at the 6th Congress of the International Association for Testing Materials, New York, 1912.

Mottled Cast Iron: Intermediate between gray and white cast iron.

Pig Iron.—Cast iron which has been cast into pigs direct from the blast furnace or its equivalent. This name is also applied loosely to molten cast iron which is about to be so cast into pigs, or is in a condition in which it could readily be cast into pigs.

Mixer Metal.—Molten cast iron which has been passed into or through a metal mixer.

Iron Castings.—Definition: Castings of cast iron.

Remarks: They are usually made from liquid iron direct from the blast furnace, or by remelting cast iron in a cupola or other furnace, or in crucibles.

Malleable Cast Iron.—Definition: Iron which is first cast as cast iron and later made malleable without remelting.

Remarks: Commercial malleable cast iron is first cast as brittle white cast iron, and is then made more or less malleable either by converting most of its carbon from the state of cementite into that of temper graphite, or by removing most of it by oxidation, or by both means jointly. In both cases the malleablizing is done by close annealing, usually in contact with an oxidizing agent. Thus there are two classes of commercial malleable cast iron, of which one owes its malleability to a large removal of carbon, and the other to a large removal of carbon from the outer part of the casting, and to the precipitation of much of the remaining carbon in the free or graphite state. It is not in accordance with good industrial usage to apply the name "steel" to any product of these malleablizing processes, or to any product made by remelting cast iron in a cupola or like furnace, and such application is generally held to be fraudulent.

Malleable cast iron differs from steel: (1) usually in containing more carbon, and (2) in being cast into a mass which is not initially malleable. Malleable cast iron is not strictly cast iron, but a distinct species, co-ordinate with wrought iron, steel, and cast iron.

Wrought Iron.—Definition: Malleable iron which is aggregated from pastry particles without subsequent fusion, and contains so little carbon that it does not harden usefully when cooled rapidly.

Remarks: Commercial wrought iron, though occasionally made directly from the ore, is usually made from cast iron by such removal of its carbon and silicon as to convert it, at the high temperature used, into pasty particles, and by squeezing these together in a bath of cinder or slag into a coherent mass which retains permanently an important quantity of that slag.

In Great Britain "malleable iron" is often used as synonymous with "wrought iron," but sometimes at the risk of leaving the lay reader in doubt whether it refers to wrought iron or to malleable cast iron. Hence we advise against this use of "malleable iron."

Steel.—See "Carbon Steel" and "Alloy Steel" below.

1. Fluid origin. Definition: Iron which is cast from the molten state into a mass which is usefully malleable initially at least in some one range of temperature. (See "Steel II" below.)

Remarks: Such metal is steel whether it can be hardened or not, whether it contains much or little or even no carbon, and for that matter even if it is chemically pure iron. It is sometimes called "ingot metal." With the exception of "blister steel" and its derivatives all the steels which have any present industrial importance including the "alloy steels" (see below) fall under this definition.

These steels have been divided into:

(a) *Ingot Iron.*—Steel with too little carbon to harden usefully on rapid cooling. This name has never been widely used, and for a long time fell into complete disuse. It has lately been revived as a trade name. It should be avoided in scientific and technical writings because, with the iron-carbon alloys divided into the four great species, (1) wrought iron, (2) steel, (3) cast iron, and (4) malleable cast iron, it is confusing to call a variety of "steel" "ingot iron."

(b) *Ingot Steel.*—Steel with enough carbon (say 0.30 per cent or more) to harden usefully on rapid cooling.

Steel made by melting in a crucible is called "crucible steel"; that made in an electric furnace is called "electric steel."

Steel II.—Plastic origin. Definition: Iron which is aggregated from pasty particles without subsequent fusion; is malleable at least in some one range of temperature; and contains enough carbon (say 0.30 per cent or more) to harden usefully on rapid cooling from above its critical range.

Remarks: Blister steel and its derivatives and a few other high-carbon steels which are unimportant today, are the only present steels covered by this definition.

Blister Steel.—Steel of plastic origin made by cementing wrought iron with carbonaceous matter. Also, commercially, such steel when heated and worked into merchant sizes. Most writers have used "blister steel" in the former and broader sense. In Sheffield it is used solely in the latter and narrower sense.

Remarks: The blister steel of commerce is made by cementing very pure wrought iron with charcoal.

Blister Bar, Cement Bar, Converted Bar.—Bars of blister steel.

Plated Bar.—Definition: Bars of blister steel which have been rolled or hammered while hot.

Remarks: This treatment which is usually applied to such bars broken to convenient lengths, flattens down their blisters and toughens the metal somewhat.

Single-shear Steel.—Definition: Shear steel made by welding a pile of plated bars into a faggot. Also the bars and other merchant shapes made by rolling or hammering such a faggot.

Double-Shear Steel.—Definition: Shear steel made by piling, hammering, and thus welding bars of single-shear steel into a bloom. Also the bars and other

merchant shapes made by rolling or hammering such a bloom.

Carbon Steel.—Definition: Steel which owes its distinctive properties chiefly to the carbon as distinguished from the other elements which it contains.

Remarks: Though among the alloy steels some are but moderately malleable, among the carbon steels industrial usage confirms the name "steel" to products malleable enough to be rolled or forged into merchant shapes.

Alloy Steels—Definition: Steel which owes its distinctive properties chiefly to some element or elements other than carbon, or jointly to such other element and carbon.

Remarks: Some of the alloy steels necessarily contain an important percentage of carbon, even as much as 1.25 per cent. There is no agreement as to where the line between the alloy steels and the carbon steels shall be drawn.

Ferro Alloys.—Definition: Iron so rich in some element or elements other than carbon that is used primarily as a vehicle for introducing that element in the manufacture of iron or steel.

Remarks: The ferro alloys are not usually usefully malleable, and they usually contain more of the tween alloy steels and ferro alloys must needs shift. With variations in industrial conditions the line between allow steels and ferro alloys must needs shift. Indeed, a substance might simultaneously be an alloy steel in the machine shop and a ferro alloy in the steel mill.

Semi Steel.—A vague trade name for various products near the border line between steel and cast iron. Among these are low carbon cast iron made in the air furnace, or in the cupola furnace by the addition of steel scrap to the charge. Also a trade name for malleable cast iron.

British Definition.

Cast Iron.—Definition: Iron containing varying percentages of silicon, phosphorous, etc., and so much carbon that it is not usefully malleable at any temperature.

Remarks: The cast iron of commerce is reduced from the ore, usually in the blast furnace, in direct contact with solid carbon, and is then tapped from the furnace in a molten state. It always contains a considerable percentage of carbon, usually from about 3.0 to 4.5 per cent, and in most cases an appreciable percentage of silicon.

(Gray cast iron, white cast iron and mottled cast iron in agreement with official report.)

Pig Iron.—Definition: Strictly speaking, cast iron which has been cast direct from the blast or other furnace into moulds of varying sizes and shapes, known as pig moulds, and allowed to solidify in the form of pigs and slabs.

Remarks: This name is also applied loosely to molten cast iron which is about to be so cast into pigs or is in a condition in which it could readily be cast into pigs.

Mixer Metal.—In agreement with official report.

Iron Castings.—Definition: Castings made by pouring molten cast iron into moulds of designed shape or form, other than in the form of pigs or slabs.

Malleable Cast Iron.—Definition: Iron which is first cast into moulds and afterwards made more or less malleable without remelting, by close annealing usually in contact with an oxidizing agent.

Remarks: Commercial malleable cast iron is first cast as brittle white cast iron and is then made more or less malleable either by converting most of its carbon from the state of cementite into that of temper graphite, or by removing some of it by oxidation. In both cases the malleablizing is done by close annealing usually in contact with an oxidizing agent. Thus there are two classes of commercial "malleable cast iron," of which one owes its malleability to a large removal of carbon and the other to a large removal of external carbon and to the precipitation of much of the remaining carbon in the free or graphite state. "Malleable cast iron" differs from steel, (1) usually in containing more carbon, and (2) in being cast into a mass which is not initially malleable. Malleable cast iron is not cast iron, but a product of cast iron; it is cast iron which has been made malleable by special treatment and is as distinct from cast iron as wrought iron or steel which are also products of cast iron.

Wrought Iron.—Definition: Iron which is produced at a temperature below its own melting point either direct, from iron ore, or from cast iron as a malleable mass by the aggregation of pasty particles without subsequent fusion. It contains so little carbon that it does not usefully harden when rapidly cooled, is soft and readily malleable within wide limits of temperature and always contains intermingled slag.

Steel.—Iron either pure or associated with other elements which has been cast from a molten state whether it hardens or not on rapid cooling from above its critical range and after solidification is so usefully malleable that it can be forged or rolled into merchant sections or shapes at least within some range of temperature; or, iron which has not been cast from a molten state and contains sufficient carbon to cause it to harden usefully when rapidly cooled from above its critical range and is so usefully malleable that it can be forged or rolled into merchant sections or shape at least within some range of temperature.

The British members of the Committee prefer the definition in the above form, but as the Committee of steel-makers suggested its division into two parts they submit it, thus divided, below, for consideration.

Steel I.—Fluid Origin. Definition: Iron, either pure or associated with other elements, which has been cast from a molten state whether it hardens or not on rapid cooling, from above its critical range and after solidification is so usefully malleable that it can

be forged or rolled into merchant sections or shapes at least within some range of temperature.

Remarks: Such metal is steel whether it can be hardened or not, whether it contains much or little or even no carbon, and for that matter if it is chemically pure iron. It is sometimes called "ingot metal." With the exception of cemented bar, blister steel, and shear steel, and a few similar steels, all steels which have any present industrial importance fall under this definition.

Steel II.—Plastic Origin. Definition: Iron which has not been cast from a molten state and contains sufficient carbon to cause it to harden usefully when rapidly cooled from above its critical range, and is so usefully malleable that it can be forged or rolled into merchant sections or shapes or shapes at least within some range of temperature.

Remarks: Cemented bar, blister steel, shear steel, and a few other high-carbon steels are the only commercial steels covered by this definition.

Blister Bar, Cement Bar, Converted Bar.—Definition: High class Swedish or other wrought iron bar of equal purity which has been subjected to a process of cementation in contact with charcoal, which process, while introducing carbon into the iron also develops blisters on the surface of the cemented bar.

Blister Steel.—Definition.—A term sometimes used to describe cemented, converted or blister bar which has been heated and worked into merchant sizes.

Plated Bar.—Definition: Blister bar or cemented bar which has been broken into suitable lengths, heated and hammered out to confer some toughness and to flatten down the blisters.

Shear Steel.—Definition: Steel made by piling and welding plated bars under a thin layer of suitable flux. The welded bars are drawn down under the hammer into a faggot which is forged into merchant sizes, and is known as "single" shear steel.

Double-shear Steels.—Definition: If the single shear steel faggot be nicked, bent back upon itself, the two parts heated, welded and again hammered down, the resulting bloom is known as "double" shear steel. The merchant sizes forged from these bloomes are also known as shear steel.

Alloy Steel, Ferro Alloys.—In agreement with official report.

Semi-Steel.—In agreement with the official report.

STEEL AND MALLEABLE CAST IRON.

Your committee is divided concerning two anomalies in present nomenclature, (1) that what is called "malleable cast iron" lacks the essential and defining property of other cast iron, lack of useful malleables at all temperatures, and (2) that what is called "blister steel" lacks the essential and defining property of other steel, its being cast from a molten state into a mass initially malleable. A part of your committee proposes but the minority opposes taking the initial steps to rid first scientific, then technical, and finally industrial nomenclature of these anomalies, by removing malleable cast iron from the class "cast iron" and blister steel from the class "steel," and giving these species new distinctive specific names. The initial step proposed is formulation in Section IV of this report of propositions touching this subject, with the purpose of bringing out the arguments for and against this plan. If after thorough discussion either or both these amendments of the classification should still seem wise, your committee would propose to offer to the Seventh, or 1915, Congress the necessary resolutions and definitions for putting these amendments into effect. Though this matter has been under discussion in a general way for nearly forty years, yet in deference to the wishes of the British members we do not ask any formal expression of opinion from the Sixth Congress.

All agree that these anomalies exist; that the only one important quality which the various varieties of cast iron apart from malleable cast iron have in common, and therefore their one defining characteristic, capable of serving to distinguish them from other kinds of iron, is that they are not usefully malleable at any temperature, whereas malleable cast iron is very malleable; and that the only one important quality which the various varieties of steel other than blister steel have in common, and therefore their one defining element, is their having been cast into a mass initially malleable whereas blister steel is not so cast. All agree that if malleable cast iron and blister steel were removed from their present classes of cast iron and steel, and given distinctive names, our nomenclature would be simplified and made more consistent, and that this greater simplicity and consistency would, taken in and by themselves, be good. But as to the expediency of taking the first steps in this direction we differ.

Were these steps once taken, the nomenclature might be given greater precision by defining "useful malleableness" quantitatively; but this further refinement might well follow the initial step of moving distinctly in the direction of qualitative consistency.

A glance at the roughly parallel case of the science of ichthyology and the fish industry may clarify the matter. They have the same ultimate purpose—to benefit man; but their means differ radically. Ichthyology must needs proceed scientifically; i. e., systematically and with precision. Its usefulness demands these conditions. Precise and consistent terminology forms a needed part of this system and precision. Consistency compels ichthyology to exclude mammals from the class "fish," and hence it excludes whale. But the fish industry stands in a radically different position. It has no need of consistency of nomenclature, based on specific characters. Hence it speaks of whale as "fish." It refuses to respect the nomenclature of ichthyology, though properly accepting everything of industrial value which that science lays bare.

But of the two, it is the ichthyologist rather than the fish industrial that gains the ear of the rest of educated

mankind through his lectures and writings. As with the secular progress of education an increasing proportion of the educated take their language from the ichthyologist, more and more adopt the scientific nomenclature which excludes whales from the class fish, first because it is the nomenclature of those who have their ear, second because they like its consistency. They come to regard as ignorant and ill educated those who think of the whale as a fish. With the further progress of the world, an increasing proportion of the captains of the industry receive an education high enough to familiarize them with the scientific nomenclature, and adopt it because of the human wish to be ranked with the educated. From like human motives the fashion thus set works down to ever lower levels. So in time by the working of natural processes the consistent nomenclature slowly displaces the inconsistent, and the revolution is complete. This is one of the mills of the gods which, though it grinds slowly, and sometimes seems to stop grinding, yet in the end surely grinds exceedingly small.

Applying these considerations to our present case, there is the metallurgical industry, and there is the science of metallurgy. Till lately the industry has dominated the science completely. The science has been little more than the direct handmaid of the industry, serving mankind only indirectly and through the industry. But the time will come and may have come already when the science must do its own independent work in its own way, as the sciences of botany, ichthyology, geology, and mineralogy do theirs. In one case as in the others the intellectual work of the science confers its ultimate material benefit on mankind through the administrative work of the industry which it directs, botany through the farming and the lumber trade, ichthyology through the fish trade, geology and mineralogy through the mining and metallurgical industries; but in one case as in the others the time comes when the science refuses to sacrifice its efficiency and its power of expressing itself to mankind apart from the industry which it serves, by submitting to inconsistencies of nomenclature which are irksome and hampering to it, however easily tolerated by the industry. In each case the degree to which the science does its intellectual and experimental work apart from the industry, and addresses itself primarily to itself and to the public and only secondarily to the industry, increases progressively and irresistibly. The science comes to demand more and more insistently that it shall be freed from inconsistencies of nomenclature. It points out that though these inconsistencies are more hampering to its work which is primarily intellectual than to the work of the industry which is primarily administrative, yet the simplifications on which it insists for its own sake will in the end be a convenience to the industry itself.

In 1876 metallurgical science made a struggle against existing inconsistencies of nomenclature, but it was too weak to succeed. The industry will always be inconvenienced temporarily by any change, however useful it may be in the end, and, naturally mindful of that present inconvenience rather than of the convenience to posterity of inheriting a consistent and convenient nomenclature, monetary system, or system of weights and measures, is likely always to oppose every such improvement, however useful. Hence the survival of pounds, shillings, and pence, and the postponement of the universal adoption of the metric system.

Without proposing the impossible task of making trade nomenclature consistent, we may now ask "Has metallurgical science grown enough stronger in these thirty-six years to enforce its demand for consistency of nomenclature for its own use, in addressing itself and the rest of mankind apart from the industry?" We believe that all other branches of science of which there are industrial applications have such a nomenclature. Has the time come when we are strong enough to erect and maintain one, or must we wait yet a while? That we shall be strong enough one day cannot be questioned. Are we today? A part of your committee believe that we are, and that we should now take the initial step already indicated.

As every body of men in enforcing their rights must respect the rights of others, so must the men of science, as the weaker party, scrupulously respect the rights of the industry. The industry naturally refuses to adopt the changes which we propose for the sake of consistency and clearness. This refusal is within its rights. It has a right to retain the existing inconsistencies. This right we must respect. Beyond this, we must do nothing likely to facilitate fraud.

In order to carry out this program we give in this present report the present names and the corresponding definitions, for present use; but we formulate propositions reciting the facts, and recognizing that the interests of science and of the public require that these inconsistencies be removed by removing the steels of plastic origin from the class "steel" and malleable cast iron from the class "cast iron." These propositions are not offered for adoption. They aim to focus the matter and bring out the arguments for and against our plan.

If reason appears to be on our side, we expect to recommend to the Seventh Congress that it advise that the resultant consistent nomenclature be used in scientific and technical writings, but to record industrial usage.

If this course is followed, a strictly consistent nomenclature and definitions will be available for scientific purposes, and yet the trade usage will not be affected except gradually as it adopts the usage of science.

We believe that such consistent nomenclature, if authorized by a body of such weight as the Seventh Congress, will be welcomed by scientific writers and teachers, because of its consistency. Taught by them through their writings and addresses to their hearers,

readers, and the public, it will be adopted gradually by technical writers because of its consistency. Because it is the fittest it will survive, and in the fullness of time will drive out the inconsistent nomenclature.

We cannot shut our eyes to the fact that the coexistence of the two different meanings of steel, based on radically different definitive properties, the "hardening power" for "steels" of plastic origin, and "fluid origin" for other steels, not only makes our nomenclature inconsistent, but causes it to shift from one inconsistency to another according to the needs of the hour. This situation offers a strong temptation to play upon these two meanings in such a way to to set a given product in the then best selling class. There are many varieties which, by this play upon meanings, may be shifted from "steel" to "iron" and back, according to which of these names is at the moment the more attractive to the public. For instance, prior to Bessemer the hardening power was the essential defining property of "steel"; but those interested in the Bessemer process disregarded existing nomenclature, set up the fluid origin as the defining property, and called all Bessemer products "steel" whether they would harden or not, "steel" being then associated in the public mind with superiority. Today the tables are turned; "iron" is associated in the public mind with superiority, and commands a higher price than "steel" of like composition. Just as in Bessemer days certain makers sought how to include their product in the class "steel," so today certain others seek, perhaps unconsciously, how to exclude theirs from that class.

Those who make a special low carbon open hearth steel exclude it from the class "steel" by adopting the hardening power as the definitive property; whereas makers of puddled steel exclude their product from the class "steel" by adopting fluid origin as the definitive property.

Both may be acting in perfect good faith. In some cases they evidently are. It is not they but the coexistence of contradictory meanings that is to blame.

As the trade refuses to be bound by its own inconsistencies, but shifts thus from one to another, playing upon the confusion which it has itself created, it is well that science should step in, select the dominant usage, and say "I will adopt this usage, and my character is warrant for its fixity; you may shift from one usage to another as you will, but with Homer's helmsman I will keep my rudder true, and because my usage is consistent and fixed you will eventually recognize it as the standard.

Turning now to the question of fraud, we have never heard that the fact that the definition of "fish," adopted by the educated world apart from the fish trade, excludes whales, has ever worked anybody a hardship, unless it is a hardship to whalers to be excluded from the caste of "fishermen"; nor can we conceive probable contingencies under which that exclusion could facilitate fraud. In the same way we fail to conceive probable contingencies under which the proposed exclusion of blister steel from the class "steel" in a strictly scientific nomenclature can facilitate fraud. If those who fear such fraud will really face the matter, and ask themselves how it can come about that fraud should result from giving a scientific definition of steel, "iron cast from the molten state into an initially malleable mass," coupled with the explanation of the industrial uses of the word "steel," we believe that they will find that this fear is not only utterly vague but groundless, a nebulous creation of their own imagination. If in any way it should suggest to the buyer of blister steel not to pay an irresponsible and unknown seller before having some reason to believe that his purchase corresponds to his needs, that does not seem to us a hardship which should forbid our making our nomenclature consistent.

To couple a statement of existing industrial usage with the strict scientific definition would prevent the use of the scientific definition for custom frauds and other legal frauds, because where scientific and industrial usage differ, the custom-laws and judicial interpretations in general are necessarily based on the accepted industrial meanings. Contracts, expressed or implied, are necessarily interpreted as being based on the meaning presumably attached by the contracting parties to their own words, and these parties, in entering into their contract, clearly must have industrial rather than scientific considerations in mind.

But beyond this, the complete prevention of fraud is not a proper function of a definition. The definition of "horse" properly includes blind, lame, and moribund horses; that of "fish" properly includes decayed fish. A lexicographer who framed his definitions in general so that they excluded from the various classes all individuals save those most useful industrially, would be as mad as the purchaser of a horse who paid for it without some reason, from inspection, from the known character of the seller, or from other sources, to believe that it was neither blind, lame nor moribund, unless blindness, lameness, and death happened to be harmless for his special purpose. Equally insane, in our opinion, would be the purchaser who paid for a given lot of steel without some reason to believe that it was of the kind which he needed, be that reason a contract expressed or implied as to its composition or properties, be it the known character of the seller, be it the brand of the steel, or be it what you please. Your committee does not understand that one of its duties is to protect the reckless from the consequences of their recklessness.

The fear that our proposition would cause confusion seems to us to rest equally on misapprehension. To fix our ideas, let us suppose for the moment that the name selected for "blister steel" were "blister metal" and that the name selected for "malleable cast iron" were "malleablized cast iron," and let us further assume that the names actually selected shall be fit, shall suggest clearly the colloquial name to which they

correspond, and shall not be likely to be confused with other existing names, whether precise or colloquial. The effect of our proposition would not be to remove the words "blister steel" and "malleable cast iron" from industrial use; to attempt that would be like trying to stop the east wind. It would simply degrade them from their present position of being part of scientific nomenclature to being current colloquialisms. The technically educated man would know that the strict scientific name "blister metal" corresponds to the colloquial name "blister steel," and the scientific name "malleablized cast iron" to the colloquial name "malleable cast iron." He might indeed continue to use the colloquial name except where precision was called for. The mere fact that a name is colloquial and not part of scientific nomenclature is no bar to its use. The speech and the informal letters of most of us abound in colloquialisms, if not in slang. Is the fish trade hampered or confused by the fact that ichthyologists call whales "mammals"? And would the steel industry be confused by our using the name "blister metal" or "malleablized cast iron" in technical writings? For a very large number of our common words strict and colloquial meanings exist side by side, and for many of our common objects accurate and colloquial names exist side by side, without causing confusion.

Experience proves that when, for purposes of a consistent scientific nomenclature, a substance is removed from the class in which it has stood till then and set in another class, no harm is done to the industry which makes or deals in that substance. Whales were removed from the class "fish" to the class "mammal"; oil of vitriol from the class "oil" to the class "acid"; carbonic and phosphoric acid from the class "acid" to the class "anhydride"; oil of wintergreen from the class "ether" to the class "ester"; black lead from the class "lead" and given a new name "graphite." In the previously existing and wider meaning of their several class names, sulphuric acid was distinctly an "oil," carbonic and phosphoric acids distinctly "acids," oil of wintergreen distinctly an "ether," and black lead distinctly "lead." But for consistency of classification, these classes were narrowed so that each became a consistent unit, by excluding the several alien substances, which were thereby transferred to new classes. These transfers caused absolutely no harm to the several industries, indeed in some cases had no effect whatsoever on the industry and were even unknown to the majority of the industrials. To this day these several substances are called in the industry by their old names to a greater or less extent.

The case of graphite is particularly instructive. Formerly confused with galena, as is shown by their both being called "plumbago" then, its true nature was not discovered till 1779 and its name "graphite" was not proposed till 1789. The name "lead" then and now colloquially and industrially included not only metallic lead, but also black, white, and red lead. Indeed for the graphite crayons of our pencils there is no familiar name except "lead," and these pencils themselves are universally called "lead pencils." Before 1789 metallic lead and graphite probably were not thought identical, but both were "lead," i. e. "lead" was a generic name. If there was any difference in the closeness with which this name was identified with these two substances, then for all we know it may have been identified more closely with graphite than with metallic lead. Exactly so, nobody thinks that blister steel is identical with steel or fluid origin, and the name "steel" has been used longer for steels of plastic than for those of fluid origin. But in the one case as in the other the need of precision and consistency in scientific nomenclature leads us to narrow the scientific meaning, that of "lead" to metallic lead, that of "steel" to fluid origin steels, for the simple reason that no other mode of narrowing it to a consistent unit offers. No reason suggests itself why the removal of blister steel and malleable cast iron from the classes in which they do not belong should do harm or cause confusion, seeing that the parallel removal of graphite from the class "lead" was harmless.

Let those who fear confusion from the co-existence of standard scientific and colloquial words and meanings ask themselves frankly whether those who habitually use colloquial words and meanings are in fact confused when careful writers write of "tin plate" instead of "tin."

Let them ask what trade was hampered or confused when whales were transferred from the class "fish" to the class "mammal," or is hampered by the fact that trade still call them "fish" and science "mammals;" or what trade is confused or hampered by removing black lead from the class "lead" and re-naming it "graphite;" or by the present co-existence of the names "black lead" and "graphite," or by the co-existence of the colloquial meaning of "lead" which includes "graphite" and the scientific meaning which excludes it? The fear is simply the fear of the unknown, the unrealized, the unimagined; the fear of every change as change, because of failure to imagine correctly the conditions which the change will actually create.

Some unfamiliar with the conditions have thought that there is an inconsistency between the attitude expressed concerning "cast iron" in the fourth paragraph of this report and the proposition to remove blister steel from the class "steel." But the slightest examination shows that no such discrepancy exists, as we will now explain.

That wrought iron and low-carbon steel must for the present continue to be distinguished by means of their origin, the plastic origin of wrought iron and the fluid origin of such steel, nobody questions. The importance of distinguishing between these two classes is self evident. We all recognize the influence of the presence, quality, and distribution of the slag of wrought iron, its facilitating welding, its increasing the plasticity under certain important conditions, its lowering the transverse ductility, etc., etc. But when

we try to frame words which shall express this difference by means of positive inherent properties as distinguished from origin we fail. He who shall frame such words will thereby open the way to a great improvement on our classification and definitions. We cannot distinguish wrought iron from such steel by its greater slag-content, for some such steel contains more slag than some such wrought iron, and so on with each of the points of difference. Collectively their importance is neither questionable nor questioned, but nobody has yet found a way of framing words which shall distinguish these two classes from each other in terms of these unquestionably important inherent properties. Therefore, awaiting the coming of the framer of such words, we must needs be content to base the distinction between wrought iron and such steel on origin, a poor way philosophically speaking, but yet a perfectly effective and good working substitute for a better, and therefore to be retained till that better appears.

This being the case the proposal to remove blister steel from the class "steel" is not a proposal to set up origin as a new basis of classification but to extend its use to the strictly analogous purpose of parting high carbon steel of fluid origin from blister steel which is of plastic origin, and thus making our classification consistent by using the same basis for low and for high carbon products.

Some say "Why should not identical properties in the case of blister steel and crucible steel of like composition cause them to be classed together?" This is a mere befrogging of the issue. We deny most emphatically such identity of properties. It may be true that for certain specific purposes such blister and such crucible steel may be equally well fitted, but that is neither here nor there. For certain specific purposes low carbon steel and wrought iron may be equally well fitted; horses and oxen may be interchangeable for plowing, nevertheless they deserve distinctive names.

If it were practicable to erase the present "origin" basis of distinction between low carbon steel and wrought iron and to use the hardening power as the basic quality of steel, we should concede the utility of discussing the relative appropriateness of the two bases, according great weight to the priority of the hardening power as a basis. But because, all admit, the origin basis must needs be retained for parting the low carbon products, and because origin is therefore the only single element available, we maintain that the use of "origin" should be extended from the low to the high carbon products, more specially because this extension of this "origin" basis to the high carbon products would cause a minimum of shifting. Puddled steel, which was formerly grouped with blister steel, has spontaneously ceased to be called puddled steel, at least in America. There remain only blister steel and its immediate derivatives, an altogether insignificant and moribund class, not made in America nor we believe to any important extent in any country except England. Moreover, this class of products interests only a very small class of men, who would not pay the slightest heed to the narrowing of the class "steel" in a strictly scientific classification so as to exclude blister steel, but would go right on calling it blister steel, and we would be no more affected than the black lead industry is by the scientific exclusion of black lead from the class "lead."

Returning now to the case of cast iron, its basic property is its unalterable brittleness, and not its origin. That of low carbon steel is necessarily and regrettably its origin. The fact that consistency can be had only by extending this basis of "origin" to the high carbon products, fluid origin steel and blister steel, furnishes no excuse for introducing origin into the definition of cast iron. Further, that to which we object is not the use of origin as a basis of cast iron, but restricting cast iron to the product of a special kind of furnace, a restriction which has nothing in common with the use of origin as the basic element in steel. We are forced to part wrought iron from low carbon steel, not by specifying the kind of furnace in which it must be made, but by fluid vs. plastic origin. Were the proposition to restrict cast iron also to material of fluid origin, it might be debatable. But the proposition to restrict cast iron to the product of a single kind of furnace appears to us indefensible.

Is it not true that, with the sole exception of metallurgy, every branch of science which is related to an industry has its own nomenclature, which co-exists with the industrial nomenclature without harm to either? Are the farmers, florists, and lumbermen harrassed because the botanist uses his more precise Latin names? Do they not purposely adopt those more precise names when they wish to be exact? Are the dealers in horses, fish, sheep, cattle, bird plumes, and the like plagued because the zoologist uses his more precise Latin names? Do they not often turn to those names when they need special exactness? Some think that, when we metallurgists who are specially interested in the science as distinguished from the art of metallurgy propose to make our own nomenclature consistent we are doing some unheard of thing. But is it not the truth that in our supineness we have deferred to this astonishingly late date the enforcement of that right which every other branch of science long ago enforced, and enforced without any harm to the allied industry, the right to a consistent nomenclature? We believe not that consistency and precision of language tend to confuse, but that to defer making language systematic and consistent is to prolong confusion.

The foregoing part of Section 3 represents the views of part of the Committee; the views of the British members are as follows:

The British Members of Committee 24 regretfully find themselves compelled to dissent from some of the most important views expressed in Section 3 of this Report prepared and therefore are obliged to state

their own views. After consultation with a special Committee of British manufacturers appointed to confer with them, they have drafted a few alternative definitions which they herewith beg to submit for consideration.

The chief points of difference in the definitions are in respect of (1) Steel: (2) Wrought iron; and of (3) Malleable cast iron. With the exception of these, they have, with a few modifications, adopted almost in their entirety the proposed official definitions and the remarks thereon.

The British Members understood that the Committee was appointed not to introduce new names in the places of old ones, but to define clearly existing terms as they are understood by technical men. They take the strongest exception to the recommendation to remove Steel of Plastic Origin from the class of Steels, and to give these and Malleable Cast Iron new names. The steels in question possess the well-known property of hardening and tempering, which until a few years ago, was regarded as the essential and distinctive property of Steel. If these recommendations should be accepted, large quantities of cutlery steel, shear steel, and other material, which have for generations been known as steel will have to be excluded, and they consider that any attempt to re-name such well-known materials would be impracticable, lead to confusion and greatly discredit the work of your Committee and that of the Association. They therefore consider it is not only undesirable but worse than useless to attempt to introduce new names for well-known products, such as Cemented Steel Bar, Shear Steel, Malleable Cast Iron, etc. With regard to the term "Malleable Cast Iron," it may be admitted that this is not in itself an ideal one, but it has become incorporated in technical literature and by common usage is now so well understood by technical men that the British members cannot see how any useful purpose would be served by altering the name; provided it is carefully defined, less confusion would, in their opinion, arise by retaining the existing term than by any attempt to introduce a new one. In England, and, so far as they are aware, on the Continent, "Malleable Cast Iron" has never been classed with cast iron, but has stood by itself, and there has never been any confusion between it and "Cast Iron" amongst technical men.

In view of the great difficulties of carrying on a discussion by correspondence with Members of the Committee in all parts of the world, and in many cases speaking different languages, the British Members are of the opinion that the detailed discussion and full consideration of the various views expressed, have not been possible to the extent necessary to enable the Members of your Committee to exercise that considered judgment, which is so essential to enable them to arrive at a decision on questions of such far-reaching importance. They therefore most strongly support the Official recommendations that the questions raised in Section 3 be fully discussed, but that the Congress should refrain from committing itself to any official expression of opinion thereon and defer action until the views and criticisms of the whole of the Members of the Committee have been further elicited.

PROPOSITIONS TO BE DISCUSSED BUT NOT VOTED ON AT THE SIXTH CONGRESS.

I. Whereas every scientific classification should be based on characteristics fit for this purpose so that all the members of each class shall have in common the defining characteristics the possession of which constitutes that class;

II. And whereas, the present classification of the products of iron and steel, however well fitted for the present industrial needs, offends this law in regard to the classes "steel" and "cast iron," first in that blister steel lacks the essential defining characteristics of all other steels, "having been cast from the molten state into an initially malleable mass" which all other steels have, and in virtue of which these other steels are grouped into the class "steel"; and second in that "malleable cast iron" lacks the essential defining characteristics of all other cast irons, viz.: that their "malleableness, if any, is below the useful limit at all temperatures," in virtue of which characteristics all other cast irons are grouped into the class "cast iron";

III. And whereas these inconsistencies hamper scientific writers and speakers seriously, and tend to confuse their readers among all educated classes, save and except only those familiar with the industry itself, and thereby to obstruct the diffusion of knowledge concerning iron and steel outside the industry;

IV. And whereas the interests of the body of scientific investigators, teachers, writers, their readers, and the public outside the industry, have become so important in the premises as to demand recognition;

V. And whereas though the systematizing of its classification by any branch of science, especially if it is related to an industry, usually results in degrading certain names, or certain inconsistent and contradictory meanings of such names, from their initial position within good usage into colloquialism; yet experience proves most abundantly that this degradation in fact works no hardship and causes no confusion in the industry, which in its current usage disregards such degradation and is not deterred in the slightest degree from continuing to apply a name by the fact that such application has thus become colloquial and not scientific; so that the benefit which science and the outside public derive from the consistency is not offset by any damage to the industry, which remains a law unto itself in regard to trade names:

VI. And whereas blister steel and the allied steels of plastic origin are of only slight importance except in Great Britain, and some of them have elsewhere spontaneously ceased to be called "steel" even industrially;

Now, therefore, it is believed:

1st, that, for the purposes of a strictly scientific nomenclature as distinguished from industrial nomenclature, malleable cast iron ought to be removed from the class "cast iron";

2nd, that, though in Great Britain the name "steel" has become so firmly attached to blister steel and the allied substances of plastic origin, that it is inexpedient to attempt now to remove them from the class "steel" in industrial, commercial, and colloquial usage, at least in that country, yet such removal is desirable for the purposes of a strictly scientific usage, which should adopt the dominant defining characteristics of "steel," the combination of malleableness with fluid origin, and reject the co-existing but inconsistent defining property, "the hardening power."

THE URANIUM AND RADIUM SITUATION.*

By CHARLES L. PARSONS.†

Some months since rumors reached the U. S. Bureau of Mines of an increased demand for carnotite ores from Colorado and that these ores were being shipped abroad in some quantity. Further, it was reported that the methods of production involved large losses of material and that methods for concentrating low-grade material now being thrown on the dump were greatly needed. Accordingly, Messrs. R. B. Moore and K. L. Kithil were assigned to the task of investigating the situation with headquarters at Denver, where the Bureau established a laboratory for the purpose of investigating the rarer metals occurring in the western part of the United States and problems bearing upon the prevention of waste and increased efficiency in the mining industry. The surprising conclusion has been reached that while all the radium placed upon the market in the last few years has been produced in Europe, a large portion of this output has come from American ores.

Radium institutes have been established in Austria, France, Germany and England, a European science and industry have been developed from American radium ores and even the uranium present with the radium has been manufactured into marketable condition only in foreign countries and returned in finished condition to our own. American hospitals and physicians have been forced to procure from abroad such radium as they could afford for experimental purposes, and investigations in our governmental and university laboratories of the wonderful properties of radium and their possible application to the eradication of disease and the development of industry have been hampered by the almost prohibitive prices at which the finished material is held.

While the Austrian government, realizing the untold possibilities of the radium ores of St. Joachimstaal, has purchased the mines, put their output under direct governmental supervision, and has entered into an arrangement whereby this ore is worked up in cooperation with the Vienna Academy of Sciences for experimental purposes in a carefully administered radium institute, America has allowed her large and much greater resources to be exploited on a basis which wastes perhaps irretrievably a large portion of the material mined, and has exported carefully selected ores at a price by no means commensurate with its radium value if worked up at home.

Even before carnotite was exported, pitchblende of the highest grade was sent out of the country at the time when the world's radium output was supposed to be coming from Austrian ores. At least 20 to 25 tons of high-grade pitchblende has been sent out of the country. Within the last two years, however, foreigners have realized the value of our carnotite resources and most of the radium that has been exported has gone abroad in this ore.

During the last year, carnotite carrying 28.8 tons of U_3O_8, from which 8.8 grains of radium chloride or 11.43 grams of radium bromide could be obtained, were produced. Practically all of this ore was shipped abroad for the extraction of radium. The value of the radium salts extracted would be at the minimum market price $528,000. The total supply of radium salts from all other sources, including the Austrian mines, was probably not more than 3.65 grams of radium chloride, basing the production of the Austrian mines for 1912 upon that of 1911, which is known.

Pitchblende, the richest of all uranium minerals, is composed mainly of uranium oxide, but also carries lesser quantities of a large number of other substances. It has been found in small quantities in Connecticut and in the feldspar quarries of North Carolina. Practically the total American output has come from the mines in Quartz Hill, Gilpin County, Colorado. The mineral is a heavy black substance which can be readily identified by anyone who will suspend a sample of the pitchblende above a photographic plate wrapped in black paper and kept in the dark for a few days with a key or other metal opaque to radium radiations placed between the sample of ore and the plate, so that when the plate is developed a shadograph of the object may identify the ore. Pitchblende may carry as high as 80 per cent uranium oxide, although the average ore is not nearly as rich.

Carnotite is a yellow mineral consisting mainly of potassium uranyl vanadate, but containing also small amounts of barium and calcium compounds. Being a uranium mineral as is pitchblende, it of necessity carries radium, although it has not yet been definitely established that the uranium and radium are in equilibrium as they are in pitchblende. However, it is known that in our western carnotite the amount of radium is not far from the equilibrium ratio and in calculations given above an allowance of 10 per cent has been made to cover this possible deficiency. While carno-

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tite is known to occur in smaller quantities in other states, the more important deposits are scattered over a considerable area in Colorado and Utah, embracing Meeker and Skull Creek, Colo., Green River, Thompson's Moab, Richardson, Table Mountain, Pahreah, and other places in Utah. The largest proportion of the ore, however, has been produced in or around Paradox Valley in southwest Colorado, from which it has to stand long hauls by pack animal or wagon to the railroad. Carnotite always carries vanadium as well as uranium and radium, but is purchased almost wholly on its radium content, comparatively little being allowed for the vanadium present.

The ore consisting of a fine grained sandstone containing yellow finely pulverulent carnotite occurs in pockets and is easily mined. As ore below 2 per cent uranium oxide cannot at the present time find a market, a considerable portion of the ore has been thrown on the dump and is now being wasted, as material of lower grade has to be discarded on account of the long haul and the fact that European buyers have set this standard as to quality. Ores of higher grade are sometimes obtained, but they occur only in small pockets and it is generally advisable to mix these high grade ores with ores of somewhat lower grade in order to increase the marketable output. Ore of 2 per cent uranium oxide is now worth approximately $75 per ton f. o. b. New York.

In the mining of these carnotite ores it is probable that 5 tons of material capable of concentration are thrown upon the dump for every ton that finds its way to market. To develop methods for concentration of these ores and save the valuable material now wasted is one of the problems before the Bureau of Mines, with fair prospect of a successful conclusion.

It is difficult to estimate the total amount of radium that has been produced up to the present time, but it is quite certain that of the ores which have been mined in this country and abroad and sold for radium production have been actually worked up into this material there is now in existence something like 40 grams (1¼ ounces) of radium. The price of radium salts varies somewhat. In large quantities it has been $60,000 per gram for both radium chloride and radium bromide, although the latter contains less metallic radium in proportion to its weight than the former. It should be remembered, therefore, that it is more advantageous to purchase radium chloride than radium bromide. In small quantities the average price has been $80,000 per gram, which represents about $2,250,000 an ounce.

The figures given show very plainly that the United States has taken the palm from Austria as the radium producing country of the world. Very few people have been cognizant of the fact that the United States has such deposits within her borders. Up to the present time very little interest has been taken in the matter and only one firm has engaged in the extraction and refining of radium in this country—a condition which is deplorable. This firm has not yet entered the radium market.

Practically every ton of ore mined in 1912 went abroad, and as the American deposits are far from being inexhaustible we are rapidly depleting our own reserve and are shipping from the country material of great value and of unknown possibilities which cannot be replaced.

The applications of radium are still too little understood to admit of definite statement. Its discovery and marvelous properties have already changed our ideas regarding the constitution of matter and scientific investigation will undoubtedly lead to valuable results which we cannot now even foresee. Altogether too many incorrect statements and vague speculations have been placed before the public as to its use in medicine. A recent report of the London Radium Institute and the many articles emanating from minor laboratories experimenting in the application of radium to therapeutics all tend to show, however, that it has a real value, the certain application of which must await further experimentation. In the meantime no credence should be given to the many stories that are sure to be printed unless they are backed up by the highest medical authority which will always give publicity with caution.

The best medical authorities appear to agree that up to the present time radium has not been proved to be specific for any disease, although it has been shown to be helpful in many cases and the outlook for its future application to certain diseases not easily treated otherwise is decidedly encouraging.

Apparently no uranium is worked up in the United States, but according to statistics gathered by the division of mineral resources of the U. S. Geological Survey, about $14,000 worth of its oxides and salts were imported into the United States in 1911. It is one of the few materials shipped abroad as ore and returned in manufactured form.

A preliminary report on Uranium, Radium and Vanadium by R. B. Moore and K. L. Kithil will soon be issued by the Bureau of Mines. This bulletin describes the carnotite deposits of Colorado and Utah and the pitchblende deposits of the former state. It also contains detail of which the foregoing is simply a general summary which cannot fail to be of value to all those interested in our mineral resources and their development.

According to the Journal of Industrial and Engineering Chemistry, the world's output of ammonium sulphate during 1912 was in tons as follows: Germany, 465,000; United Kingdom, 379,000; United States, 155,000; France, 68,500; Belgium, 49,500; other countries, 170,000; total, 1,287,000.

Olive oil produced in Austria last year totaled 1,609,064 gals., while the output in 1911 and 1910 was 1,956,921 and 820,787 gals., respectively.

AMERICAN RESEARCH WORK ON RAILS, CONDUCTED JOINTLY BY RAILROADS AND STEEL MANUFACTUERS.*

By M. H. WICKHORST.

Several years ago the number of rails in the United States that failed to give normal service or broke under moving trains became alarmingly large. The worst condition was reached about 1905. The circumstances so agitated the executive officers of the railroads that the matter was made the subject of an investigation by the American Railway Association, an organization of railroads dealing with matters of railroad operation of common interest.

Reliable general statistics are not available to show numerically the exact condition as regards rail failures, but an idea may be obtained from the report of one road that, of a lot of 10,000 tons rolled and put in the track, 22 per cent were removed during the first year on account of depressions in the head. When broken apart the majority of these rails showed interior openings in the head running lengthwise of the rail. Happily, that extreme state of affairs has passed.

RAILROAD CONDITIONS.

The wheel-loads of the rolling equipment, locomotives, passenger cars and freight cars had been rapidly increasing for twenty years or more. H. V. Wille has shown that the average total weight on drivers increased from about 69,000 pounds in 1885 to over 180,000 pounds in 1907, and reached a maximum of 316,000 pounds in that year. The average axle-load increased from 22,000 pounds in 1885 to 48,000 pounds in 1907. Since then the axle-loads have still further increased.

During the same period the weight of rail (in main-line track) increased from about 65 to 75 pounds per yard to 85 to 100 pounds per yard, which are also now the prevailing weights. The moments of inertia increased from about 15 to 20 to about 30 to 45. At the time the American Society of Civil Engineers adopted standard sections, in 1893, 80-lb. rails were just coming into use. Considered as a girder the strength of the rail increased about at the same rate as the axle-load increased, the unit-stress in tension remaining about the same, or even decreasing slightly. The unit-stress in compression, however, increased almost as the axle-load increased, as the average width of rail head increased only from about 2⅜ ins., and the diameter of the wheels has remained about the same.

STEEL MILL CONDITIONS.

While the railroads were thus busy increasing the capacity of their motive power and cars, the steel mills were likewise endeavoring to obtained increased "tonnage." These efforts took the form of eliminating unnecessary delays, installing larger converters and more powerful machinery, and using larger ingots, and sometimes, of allowing less time for the chemical reactions. At the height of the "tonnage" endeavor in the rail mills, about five years ago, there was considerable rivalry between the different mills to produce the greatest tonnage, and it reached a condition that might almost be termed madness; that had only secondary regard for the quality of the product. The purchaser had the choice of buying rails as made by the mills or going without them.

Recently, however, there has been a happy change, so that quality is being given due consideration and mutual consultations are taking place. The change was due, presumably, to the chastening effect of slack orders for rails and the present state of public opinion.

INVESTIGATION BY THE RAILROADS.

In 1906, the American Railway Association took the matter in hand through its committee on standard rail and wheel sections, which committee made a report in 1908 submitting some new designs for rail sections and also offering some tentative specifications. The matter was then referred to the American Railway Engineering and Maintenance of Way Association, now called (since April 1911) the American Railway Engineering Association.

The prevailing type of failure seems to have been the "split head", generally termed "piped rail"; the rails developed internal cavities, mostly in the head, running lengthwise of the rail for distances of several feet or more. It seems to have been the prevalent opinion that this and other types of failure, as well as poor wear, were due partly to internal structural defects and partly to finishing the head of the rail at too high a temperature. It was argued that the flanges were too thin, cooling quickly in the rolling, and that a temperature necessary to finish the flanges properly left the temperature of the head unduly high.

The remedy suggested was to make the flanges thicker, thus allowing of more uniform finishing temperature throughout the section. W. R. Webster wrote in 1901 as follows: "The cause of the trouble is now well known, it being due to the large mass of metal in the head carrying the heat so much longer than the thin metal in the flanges, thus preventing the work of rolling on the head at sufficiently low temperature to break up the coarse grain and produce the tough, good wearing rails desired." The committee of the American Railway Association later shared this same view to a large extent, as evidenced by the fact that the main feature of the rail designs they presented was the greater thickness of the flanges.

Recent work, which will be referred to later on, indicates that from the standpoint of safety high temperature of rolling is not detrimental, and that few, if any, failures can be attributed to this cause. I am re-referring now to split-head failures in bessemer rails, as this was the prevailing type of failure, and open-hearth steel had not yet come into extensive use. The recent work has also shown that such failures occur almost entirely in badly segregated metal from the top part of the ingot, attended perhaps with laminations

*From a paper presented at the 6th Congress of the International Association for Testing Materials.

and slag seams. Under pressure the top of the head of the rail spreads sideways, and, as the interior of the head with such metal as referred to cannot likewise extend laterally, it develops a crack, which grows until failure results. Of course, increase of pressure would hasten the development of such failures.

It had indeed been more or less definitely recognized that split heads occurred mostly in rail from the upper part of the ingot, but the blame was placed on internal structural defects. The trouble is now well known, it being due to the large mass due to blowholes and pipes in that part of the ingot; the role of segregation was but vaguely recognized. In Europe the part played by segregation had probably been more definitely worked out years before, but the results of that work seem to have been overlooked, or, at any rate, their importance not fully appreciated in America.

ARRANGEMENT OF RECENT WORK.

As stated, the matter was turned over in 1908 to the American Railway Engineering Association to continue the work of investigation. This association appointed a committee, which continued the investigations started by the committee of the American Railway Association, and which also made a co-operative arrangement with the manufacturers of steel rails by which the latter furnish the material and facilities of their mills for research work, and the railroads furnish the engineer to conduct the tests under the direction of their committee and publish the results. The writer was honored by selection for the position of engineer of tests, and entered upon his duties February 1, 1910. The full reports of the work done in 1910, together with other matter collected by the committee, are published in the "Proceedings of the American Engineering Association," 1911, Part 2, and it is expected that the reports of the work done in 1911 will appear in the Proceedings for 1912. Herewith are indicated some of the main results obtained, but those specially interested are referred to the above proceedings for the full reports.

SEGREGATION AS INFLUENCED BY SIZE OF INGOT.

An investigation was made of ingots of bessemer steel of various sizes from 12x12 ins. to 25x30 ins. at the bottom, all about 5 ft. high, weighing from 2000 to 10,000 lbs. As part of the investigation a chemical survey was made of these ingots to determine the distribution of the various elements, particularly as influenced by the size of the ingot.

The regions of negative segregation—that is, decrease of phosphorus below the average of the steel as poured—are also of considerable interest. The top of the ingot shows considerable decrease of the phosphorus, carbon and sulphur, and this decrease extends downward along the sides a greater distance in the larger ingots. The analyses also showed that the amount of the deficiency in phosphorus increased in a general way as the size of the ingot increased. This means that the outer parts of the section of a rail made from the upper end are softer than the average of the steel from that ingot, and this has been found true of rails examined by means of tensile tests. There is also a region of milder negative segregation in the interior and lower part of the ingot.

DUCTILITY OF RAILS.

A comparison of the ductility of rails made by the ordinary bessemer process, as measured in the drop test and in the tension test, is interesting.

In the tension test the exterior metal (as represented by the flange and the corner of the head) shows good ductility along the whole rail-bar, although there is a general increase as we go down the ingot, from about 14½ per cent elongation at 10 per cent from the top, to about 18½ per cent elongation at 90 per cent down. The results from the interior of the head near the web, however, differ considerably from these. There is fair ductility near the top, the elongation then drops off to less than 5 per cent at about 15 per cent from the top, and it then rises again, and in the lower part of the rail-bar averages slightly above the results from the exterior of the section.

In the drop test with base in tension, the elongation runs from 12 per cent to 24 per cent. With the head in tension there is also a continuous increase in going down the ingot, but the differences in elongation are much greater (8 per cent to 27 per cent). In this respect there is considerable similarity between the ductility measured in the tension test of samples from the interior of the head and the ductility as measured in the drop test with the head in tension. It would seem, therefore, that this latter test may be more useful to ascertain the ductility of the interior metal than the drop test with the base in tension as is usual in inspection work. Since the above was first written the "Railroad Age Gazette" (December 8, 1911, p. 1176) has abstracted an article by C. Frémont in "Le Génie Civil," in which Frémont comes to about the same conclusion, but goes a little farther and recommends that some of the top of the head be first planed off and the rail then tested by the drop test with the head in tension.

A Government bulletin entitled "The Utilization of Waste Raisin Seeds" has recently been issued by the Bureau of Plant Industry. It is based on an investigation which proved that the seeds removed from raisins yield technically useful products that fully justify the expense involved in separating them. The investigation described in the bulletin showed that four important products can be obtained from the waste seeds, namely, sirup, fixed oil, tannin extract, and meal. If the entire annual output of 3,000 and 4,000 tons of seed were used there would be obtained 550 to 740 tons of sirup, 340 to 460 tons of fixed oil, 330 to 445 tons of tannin extract, and 1,600 to 2,200 tons of meal.

METHOD OF ANALYSIS USED IN THE LABORATORIES OF THE ARMOUR INSTITUTE OF TECHNOLOGY.

Soap Analysis and Identification of Fats and Fatty Acids.

In preparing soap for analysis, the dried outer skin should be removed and the interior portion shaved up. All samples sould be weighed out from these shavings as quickly as possible, and the shavings preserved in a tightly stoppered bottle.

Moisture.—Five grams shavings are heated to a constant weight at 102 to 100° C. (two to three hours required). The loss is assumed to be moisture, although volatile oils are sometimes given off and any free NaOH may take up CO_2.

Total Alkali.—(See also "Total Fatty Matter.") Five grams soap are incinerated in a platinum dish, dissolved in water, boiled, and filtered if necessary. Any insoluble residue is ignited and weighed as insoluble minerals. The filtrate is made up to 250 cc. and designated solution "A." (Note—Acid liquor from total fats may be used in place of solution "A" for total alkali and silicates). Fifty cc. of solution "A" are titrated with N_2HCl, using methyl orange as indicator. The total Na_2O is calculated. If potash is present as in liquid or soft soaps, the sodium and potassium may be separated in the regular way by precipitating the heavy metals with ammonia, ammonium oxalate and corbonate, filtering, taking to dryness and igniting gently, filtering again into a weighed platinum dish, taking to dryness and igniting gently the KCl and NaCl. After weighing, $H_2P + Cl_6$ is added in slight excess and evaporated to a sirupy condition. The soluble sodium salt is filtered or decanted off the heavy yellow crystals of $K_2P + Cl_6$ which is dried and weighed.

Salt.—Fifty cc. of solution "A" are neutralized with the calculated amount of standard HNO_3 and titrated with standard $AgNO_3$ using 1 cc. of 10 per cent $K_2CrO +$ solution as an indicator. The silver nitrate solution is made by dissolving 29.048 gms. pure $AgNO_3$ in 1 liter water, 1cc. equals .01 gm. NaCl.

Silicates.—Fifty cc., solution "A," are made acid with HCl and evaporated to dryness, taken up with dilute HCl, taken to dryness again if necessary, again digested with dilute HCl, filtered and washed. The precipitate is ignited as SiO_2 and is usually calculated to Na_2SiO_3.

Sulphates.—The filtrate from the silica above is treated with excess $BaCl_2$, boiled, filtered, washed and ignited as $BaSO_4$; $BaSO_4 \times 16094 = Na_2SO_4$.

Free Alkali.—Two grams of soap are dissolved in about 100 cc. pure alcohol previously neutralized to phenol phthalim. A gentle heat aids the solution. Any precipitate is filtered off and washed with neutral alcohol. The filtrate is titrated with $N_{10}HCl$, using phenolphthalim as an indicator. The per cent free NaOH is calculated.

Free Sodium Carbonate.—The residue from the above filtration is dissolved in hot water and titrated with $N/_{10}HCl$, using methyl orange as indicator. The amount used is calculated to Na_2CO_3.

Combined Alkali.—This is the difference between the total alkali and the Na_2O in both free caustic and carbonate, or may be obtained by diluting the solution from free caustic with water and titrating with $N/_2HCl$, using lacmoid as indicator. The first is the usual and better method.

Free Fat and Unsaponified Oils.—Five grams of soap are dissolved in hot water and the solution extracted with three portions of petroleum ether. The ether is extracted with water, placed in a weighed beaker and evaporated on a water bath. The residue consists of unsaponified oils. If fats and fatty acids are to be separated from unsaponifiable oils, this residue is boiled under a reflux condenser with a measured quantity of alcoholic KOH. The excess of alkali is titrated and that absorbed by the fat calculated to oleic acid. This is subtracted from the total residue and the remainder called unsaponifiable oils.

Total Fatty Matter.—Five grams soap are dissolved in hot water as above. (Note.—The solution from the free fat may be used to get "combined fat." The sum of the two is then "total fat.") If some does not dissolve it may be filtered through a gooch, and the residue dried and weighed as insoluble matter. The filtrate is made acid with dilute H_2SO_4 or if the solution is to be used for total alkali, 40 cc. $N/_1H_2SO_4$ are used. The mixture is heated on the water bath till the fatty acids have separated in a clear layer. If desired, 5 gms. of pure paraffine, stearic acid or beeswax may be added to harden cake. The weight is deducted later. The beaker is cooled to harden the cake, warmed to get the last traces of fat on the surface, and cooled in ice water. The cake is carefully removed and washed with cold water. The water solution and washings of the cake are extracted with petroleum ether twice; the ether extracted with water, and both ether and cake dried at 100° till free from water and weighed as total fats. These are saved for further identification. The water extract is used for glycerine determination.

Glycerine.—The water solution from above is neutralized with excess $BaCO_3$, the solution boiled and filtered into a 250 cc. flask. A crystal of silver

sulphate and a few drops of basic lead acetate are added to the filtrate which is made up to the mark and shaken thoroughly. This solution is filtered through a dry filter. Fifty cc. (or any aliquot) of the filtrate are placed in an Erlenmeyer flask and excess of standard bichromate and 50 cc. of 50 per cent H_2SO_4 added. (Bichromate is made by dissolving 37.430 gms. pure $K_2Cr_2O_7$ in water and diluting to 1 liter; 1 cc. equal .005 gm. glycerine.) The solution is boiled on the water bath for one hour, diluted to 250 cc., and the excess bichromate titrated with standard ferrous ammonium sulphate, using potassium ferricyanide as an external indicator. The disappearance of the blue is the end point. The ferrous ammonium sulphate is made by dissolving 2 gms. in dilute sulphuric acid and diluting to 1 liter; 1 cc. = 1 cc. bichromate. The reaction of bichromate on glycerine is as follows: $3C_3H_5(OH)_3 + 7K_2Cr_2O_7 + 28H_2SO_4 = 9CO_2 + 40H_2O + 7K_2SO_4 + 7Cr_2(SO_4)_3$. Sugar interferes as it also reduces bichromate and in such a case the glycerine must be distilled in a current of steam before the determination can be made.

Other determinations on soap may be made as necessary such as starch and gum which would be found in the residue from the alcohol solution; carbolic acid which is dissolved in excess alkali; soap precipitated with brine and the carbolic acid in the filtrate reprecipitated with acid and measured. Sugars are usually determined with Fehling solution; alcohol is distilled, the specific gravity of the distillate taken and the alcohol calculated.

There are other determinations which are made in special cases such as borates and tar but each case must be examined individually and methods devised to meet the different combinations.

Identification of Fats and Oils.—If sufficient of the fat, fatty acid or oil is at hand, the specific gravity is determined best by the use of a pycnometer. In case only a small quantity is at hand, a drop may be placed in water in a tall cylinder and alcohol added and shaken up till the drop will remain motionless wherever placed in the mixture. The specific gravity of the dilute alcohol may then be taken and assumed to be that of the fat. All specific gravities are calculated to 15.5° C. and the mean correction is .00064 per degree Centigrade. For accurate work, tables should be consulted for individual oils or fats. For solid fats the determination is frequently made at 100° C.

Index of Refraction.—This most important determination should be made with a standard instrument such as the Zeiss-butyro or the Abbé refractometer and preferably at standard temperature of 15.5° C. for oils and 40° C. for fats. The average correction factor is .000365 per degree Centigrade. The index of refraction decreases with increase of temperature. This determination is most valuable as only a very small quantity of the fat or oil is required, and the result is obtained accurately and quickly.

Liter Test.—Seventy-five grams of fat are saponified in a metal dish with 600 cc. of 30 per cent NaOH and 75 cc. of 95 per cent alcohol. The mass is boiled to dryness with constant stirring to prevent scorching. The dry soap is dissolved in a liter of water and boiled to remove alcohol. In case soap is the original product 100 gms. of soap may be used and started at this point. One hundred cc. of 30 per cent H_2SO_4 are added to free the fatty acids and the solution boiled till a clear transparent layer forms. This is washed with boiling water till free from H_2SO_4 collected in a small beaker and warmed till the residual water settles out. The layer of fatty acids is decanted into a dry beaker filtered through a hot water funnel and dried 20 minutes at 100° C. When dry, it is cooled to about 20° above the expected liter, transferred to the liter tube (1x4 in.) which is firmly fixed through the stopper of a wide-mouth bottle (2.8x6 in.). A special thermometer for liter work is suspended in the tube so that it can be used as a stirrer. The mass is slowly stirred until the mercury remains stationary for 30 seconds. It is then allowed to stand quietly in the center of the mass and the highest point to which the mercury rises is recorded as the liter of the fatty acids.

Iodine Absorption.—There are two solutions of iodine used in measuring the iodine absorption, the Hübl and Hanus solutions. While the results are fairly close, yet for accurate work the solution used should be specified.

(1) Hübl's iodine solution—26 gms. pure iodine are dissolved in 500 cc. of 95 per cent alcohol, 30 gms. mercuric chloride are dissolved in 500 cc. alcohol and the two solutions mixed.

(2) Hanus iodine solution—13.2 gms. iodine are dissolved in 1,000 cc. pure glacial acetic acid, warmed if necessary. About 3 cc. bromine are added when cool.

A standard thiosulphate is required. This is prepared by dissolving 24.8 gms. of the pure salt in 1 liter of water. It is standardized against $N/_{10}$ bichromate (4.9083 gms. per liter) by liberating iodine from 10 cc. of 5 per cent KI with 20 cc. of the bichromate. Five cc. HCl are added and the liberated iodine titrated, using starch as an indicator.

For the determination, about .25 gm. of oil or .5 gm. fat is accurately weighed on a water glass and placed in a 16-oz. glass-stoppered bottle. This is dissolved in 10 cc. chloroform and a large excess of the iodine solution added (40 to 50 cc.). For the Hübl method, the mixture is allowed to stand 3 hours in a dark place with occasional shaking and for the Hanus method, 30 minutes, at the end of the required time, 20 cc. of 15 per cent KI for the Hübl and 10 cc. for the Hanus, are added and excess iodine titrated with thiosulphate. Starch paste is added at the end of the titration and the end point is taken when violent shaking fails to produce any recurrence of the blue color. Blanks must be run for each determination, using the same amounts of reagents without the fat,

as the value of the iodine solution changes rapidly. The weight of iodine absorbed divided by the weight of the sample times 100 gives the "iodine number."

Saponification or Koettstorfer Number.—About 5 gms. of fat or oil are weighed in a clear dry Erlenmeyer flask of 250 cc. capacity. Fifty cc. of alcoholic KOH (40 gms. KOH in a liter of pure redistilled alcohol) are added and the flask boiled under a reflux condenser for 30 minutes. The flask is cooled and the excess KOH titrated with $N/_2HCl$, using phenolphthalein as indicator. The KOH must be standardized against the HCl for each determination. The saponification number or milligrams of KOH required to saponify a gram of fat, is calculated.

The above methods give the most important constants of oils, fats or fatty acids. There are, however, special identification reactions for individual oils which would require too much space to enumerate. If the above constants are determined accurately, the oil may be placed with fair accuracy and the identification checked by some special reaction.

TABLE I.

Oilseeds.	1911 Imports. Tons.	1911 Exports. Tons.	1911 Consumption. Tons.	1912 Imports. Tons.	1912 Exports. Tons.	1912 Consumption. Tons.
Arachide (42 per cent oil)	70,143	.....	70,143	69,870	.....	69,870
Cocoa (50 per cent oil)	50,853	180	50,673	55,085	260	54,825
Copra (63 per cent oil)	148,066	6,332	141,731	183,258	951	182,307
Cotton (18 per cent oil)	155,785	2,337	153,448	214,097	1,802	212,295
False flax, oil radish, and hudge mustard (27 per cent oil)	2,831	1	2,827	2,681	38	2,643
Hempseed (25 per cent oil)	5,686	2,096	3,590	7,320	3,171	4,149
Illipe, shea nuts, mowra, and soya and castor beans (46 per cent oil)	90,640	.....	90,640	125,225	.....	125,225
Linseed and linseed meal (32 per cent oil)	276,343	6,338	270,005	330,093	5,399	324,694
Madia, kapok, niger, beechnuts, laurel berries, ben nuts, and earth almonds (25 per cent oil)	949	.....	949	311	....	311
Mustard (30 per cent oil)	7,329	228	7,101	7,209	272	6,937
Palm kernels (45 per cent oil)	250,664	.....	250,664	261,105	.....	261,105
Poppy and sunflower (32 per cent oil)	26,713	.....	26,713	16,403	.....	16,403
Rape (33 per cent oil)	134,180	6,984	127,196	125,684	7,096	118,588
Sesame (46 per cent oil)	101,672	.....	101,672	99,282	.....	99,282
Total	1,322,154	24,499	1,297,655	1,497,923	18,989	1,478,934

GERMAN TRADE IN VEGETABLE OILS.

The U. S. Consular General at Hamburg in a recent consular report states that the German oil-crushing industry moves steadily onward, in sympathy with commercial development in the primary markets which supply seeds, and aided by the general demand for oil and greases throughout the world. In the single item of palm-kernel oil German shipments to the United States in 1912 reached a value of $2,819,338, as against $2,601,631 in 1911 and $1,686,846 in 1910.

TABLE II.

Oils.	1911 Domestic production. Tons.	1911 Imports. Tons.	1911 Exports. Tons.	1911 Consumption. Tons.	1912 Domestic production. Tons.	1912 Imports. Tons.	1912 Exports. Tons.	1912 Consumption. Tons.
Arachide	29,460	523	7,221	22,762	29,345	1,261	11,706	18,900
Castor	(1)	9,511	.....	9,511	(1)	10,290	.....	10,290
Cocoa	25,336	67	3,508	21,895	27,412	62	3,581	23,893
Copra	89,293	2,392	8,997	82,688	114,854	396	18,319	96,931
Cottonseed	27,621	21,742	.....	49,363	38,213	32,321	.....	70,534
Cotton stearin	.....	207	.....	207	.....	185	.....	185
False flax, oil radish, etc	763	.....	.....	763	714	.....	.....	714
Hempseed	897	.....	.....	897	1,037	.....	.....	1,037
Linseed	86,402	2,865	3,250	86,017	103,902	31,017	953	133,966
Mowra, shea, and other vegetable	(1)	1,064	.....	1,064	(1)	1,303	6	1,297
Mustard	2,130	.....	.....	2,130	2,081	.....	.....	2,081
Niger, beechnut, madia, corn, foot, nutmeg, butter, laurel berry, etc	238	7,000	.....	7,238	78	6,332	.....	6,410
Oleic acid and dregs	.....	14,552	718	13,834	.....	13,798	1,092	12,706
Olive:								
Pure	.....	257	.....	257	.....	4,316	208	4,108
Sulphur	.....	3,468	.....	3,468	.....	5,832	.....	5,832
Olive and other similar, not in casks	.....	582	342	240	.....	646	403	243
Palm	.....	12,935	116	12,819	.....	14,183	77	14,106
Palm kernel	112,799	164	38,859	74,104	117,632	7	32,311	85,328
Poppy and sunflower	8,548	.....	.....	8,548	5,249	.....	.....	5,249
Rapeseed	42,074	764	5,738	37,100	39,134	721	2,406	37,452
Sesame	46,769	836	.....	47,605	45,670	673	.....	16,343
Soya and other beans	41,694	18,046	1,238	58,502	57,604	13,308	1,087	69,825
Wood	.....	8,678	.....	8,678	.....	6,818	.....	6,818
Total	514,024	105,653	69,987	549,690	582,925	113,472	72,149	654,248

(1) Included with "Soya and other beans."

Cotton seed imports in Germany amounted to only 52,528 tons in 1908 and increased to 214,097 tons in 1912. Copra imports in 1908 amounted to 83,668 tons and increased to 183,258 tons in 1912. Thus throughout the list of oil-making materials imports increase, or if they fail to do so the fact may be explained by crop conditions.

In preparing this year a table showing the total production and consumption of oils in Germany the percentages of oil in the various raw materials as used heretofore have been amended upon the advice of Harburg crushers, and cocoa beans and oil have been added to the list. Table 1 shows the average content of oil of the various oleaginous products, and the German imports and exports in metric tons of 2,204.6 lbs., the difference, or net imports, representing the domestic consumption.

On the basis of the average content of oil in the various seeds, Germany's production of vegetable oils in 1912 amounted to 582,925 metric tons, against 514,024 tons in 1911. This production, the domestic consumption, and Germany's foreign trade in such oils during the last two years appear in Table II.

Preliminary figures of the world's production of spelter in 1912 give the total as 962,490 long tons (of 2,240 lbs.), as follows: United States, 309,560; Australia, 2,260; Austria and Italy, 19,295; Belgium, 197,045; France and Spain, 71,025; Germany—East, 166,425; West, 100,370; Netherlands, 23,555; Norway, 8,000; Poland, 8,625; United Kingdom, 56,330.

The chemical analysis of rubber must be supplemented by physical and mechanical tests. Yet, even if the latter methods of testing should further be developed, the chemical analysis will retain its value, since the analysis seems to be destined in the first instance to allow of drawing conclusions as to the durability of a rubber material.

Rubber-tree tapping by a series of small borers set in a circle has been devised by a Dr. Christy, a British expert now in the Belgian Kongo, and is expected to cause double the results secured by tapping on the vertical incision system.

Wood pulp imports into the United States have grown from 112½ million pounds in 1901 to 1,980 million pounds last year, while British imports increased from 995 million pounds to 2,073 million pounds

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A number of prominent Japanese business men have arranged to establish near Yokohama a plant for the manufacture of steel tubes and tubing.

NEW JUTE SUBSTITUTE.

The English Textilose Manufacturing Co. has erected large works in Trafford Park, Manchester, England, for the production of textilose, the new jute substitute. The Manchester Guardian stated in a recent issue: Textilose appears to have succeeded in more thoroughly attracting expert attention than any other jute substitute yet put forward. The Austrian rights of making the new product, which is manufactured from paper yarn and cotton waste by a patented process, were acquired some time ago by the Austrian Jute Cartel, which is erecting a plant. A license has also been granted to a Belgian firm, while a commission appointed by the German Jute Cartel is now engaged in investigating the merits of textilose with a view to purchasing the German patent rights. It has been reported that a plant is to be built in Spain, capable of turning out 12,000 kilos (26,455 pounds) of textilose yarn per day, and that an international syndicate, in which French banks are largely interested, is negotiating for the patent rights in all countries where they have not alrady been disposed of. It would seem, therefore, that those in a position to judge have satisfied themselves that textilose is of practical value, even if it should not be capable of replacing jute for all purposes.

THE 1913 CUBAN SUGAR OUTPUT.

According to the U. S. Consul General at Habana, conditions in February indicated that the sugar output of 1913 will be by far the greatest in the history of the industry in Cuba. A statement of production, which carried the figures to Feb. 3, showed a total of 397,988 tons as the output of 166 mills, this result being 107,239 tons larger than to a similar date in 1912, when 165 mills were grinding cane. It is known also that several other mills will commence operation soon, and therefore if the present rate of production continues and the weather is favorable in the spring months it is entirely possible that a total output of 2,200,000 tons will be reached. This would represent a gain over last year of about 11 per cent. However, it is aparent in many of the cane districts that much of the cane will remain uncut, this being due to scarcity of labor and to a surplus of the product. Furthermore, at the prevailing prices offered for Cuban sugars delivered in New York there is not much incentive for the mills that are not so well equipped to operate, and as a consequence many of the cane growers will not be able to sell their cane. An increase in the price of sugar seems to be expected by all, however, and that may relieve a situation which does not appeal favorably to a substantial percentage of the producers in Cuba. The weather has been very favorable for the cane, and were labor more plentiful it is assured that under a normal price for Cuban sugar the industry would be thriving as never before.

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NOTES AND COMMENTS.

An Epoch Marking Food Law Decision.

Through Mr. Chas. W. Dunn, a New York attorney, who is an expert in food and drug law matters, we learn that the Supreme Court of the United States handed down a decision on April 7, 1913, that will have a greater influence on the food and drug law situation, in respect of the relations of the states to the federal government, than any other act or decision yet made. This decision was delivered by Mr. Justice Day, all the other eight justices concurring, on the appeal of George McDermott and T. H. McGrady, who had been convicted, in the Wisconsin state courts, of having violated a state labeling law. It was shown that the product ("Karo" Corn Syrup) was labeled in accordance with the federal law, and the Supreme Court has decided that the original package is that which reaches the consumer; and that products shipped from without the state to the retailer are not within the purview of the state laws. Thus it would seem that at one stroke the whole situation is changed and no manufacturer whose goods enter into interstate commerce need pay *any attention whatever* to state laws provided his goods are not adulterated or misbranded within the meaning of the Federal Act. This is truly a consummation devoutly to have been wished.—American Perfumer.

Parcel Post Service for Many Liquids Which Had Been Barred as Inflammable.

Since the adoption of the parcel post service at the beginning of the year, the question of extending it for the transmission of paints, varnishes, oils and other liquids, either as samples or in small containers, for sale to the consuming trade, has attracted widespread attention throughout the oil, paint and drug trades, and the subject has received frequent consideration in our columns. The Postoffice Department recognized the reasonableness of a more liberal attitude on liquid commodities in general, and on Feb. 24 last the parcel post regulations were amended by extending the weight on this class of matter from 12 to 16 ounces. This ruling, however, did not apply to certain liquids which were held in the non-mailable class as inflammable, in which category were included paints, varnishes and many of the oils. The restriction against these articles has now been materially modified by an order under date of April 29, permitting the transmission by parcel post under prescribed rules and regulations of those liquids having a flash point above 80° F. This ruling will extend the service to many of the products which had been under the department's ban, by which limitation manufacturers of and dealers in the articles in question had been cut off from a fair participation in the advantages of the service, as many of the so-called inflammable liquids were far below the danger point, as recognized by the recent order. The department's action is especially gratifying to the Reporter, which has realized that the exclusion of these materials from the parcel post was operating with disparaging effect to the interested trade, and we have been zealous in urging upon the postal authorities a more reasonable consideration of the protests of the affected industries.—Oil, Paint and Drug Reporter.

Parcel Post Service Extended to Paints, Varnishes, Oils, Etc.

In the efforts made by the Postoffice Department to solve the question of transmission in the mails of paints, varnishes, etc., which were held by the Department to be non-mailable as inflammable articles, the department has revised its rules on this subject, states the Oil, Paint and Drug Reporter, and now issues an order, under date of April 22, authorizing the transmission through the mails, under certain prescribed rules and regulations, by parcel post, liquids not giving off inflammable vapors below a temperature of 80° F.

It will be recalled that upon a report made by the officials of the Department of Agriculture, at the request of the Postoffice Department, paints, varnishes,

etc., were held to be non-mailable as inflammable articles and many protests were received from manufacturers of paints, oils, varnishes, etc., who desired to ship through the mails samples of their products. It is upon the representations made that many of these articles were far below the dangerous point that the Postoffice Department, through the office of Second Assistant Postmaster-General Joseph Stewart, issued the following order directed to postmasters and others concerned:

Referring to the inadmissibility to the mails of inflammable materials, as prescribed in section 494, postal laws and regulations, as amended February 23, 1910, it has been decided that inflammable liquids include any liquid or liquid mixture that gives off inflammable vapors at or below a temperature of 80° F.

Therefore, liquids having a flash point higher than 80° F. may be accepted for transmission in the mails when packed for mailing, as provided in section 22, parcel post regulations, as amended March 17, 1913, but such materials having a flash point at or below 80° F. are not mailable.

Attention is invited to the penalty prescribed in paragraph 1, section 494, postal laws and regulations (section 217 of the criminal code), for a willful violation of this law.

It will be observed that the foregoing order makes no detailed specifications as to the circumstances under which mailable liquids may be sent through the mails except that they must be in accordance with the provisions of section 22 of the parcel post regulations.

Section 22 of the parcel post regulations covers admissible liquids, oils, etc., and is in three paragraphs covering the mailing of such products when in glass bottles and when in metal containers. The full details of section 22 are as follows:

Sec. 22. Admissible liquids and oils, pastes, salves or other articles easily liquefiable will be accepted for mailing, regardless of distance, when they conform to the following conditions:

2. When in glass bottles the quantity must not exceed 12 ounces liquid measure. The bottle must be very strong and must be inclosed in a block or tube of metal, wood, papier-mache, or similar material; and there must be provided between the bottle and the block or tube a cushion of cotton, felt, or other absorbent. The block or tube, if of wood, must be at least three-sixteenths of an inch thick in its thinnest part; if of papier-mache or similar material, it must be at least one-eighth of an inch thick for bottles holding two ounces or less and at least five-thirty-seconds of an inch thick for bottles holding more than two ounces. The block or tube must be rendered water tight by an application of paraffine or other suitable substance.

3. When in a metal container, the weight of the parcel must not exceed eleven pounds. The container must be hermetically sealed and inclosed in a strong box and securely wrapped.

Under this order by the department materials having a flash point at or below 80° F., are not mailable, but above that register they may be transmitted through the mails if sent in accordance with the regulations prescribed in section 22 above.

Sampling of Coal Deliveries.

Large users of coal will be interested in Bureau of Mines Bulletin No. 63, "Sampling of Coal Deliveries, and Types of Government Specifications for the Purchase of Coal," which has just been issued. The Federal Government, which purchases $8,000,000 worth of coal annually, buys more than half of it under specifications and has gone deeply into the question of sampling and analyzing coal. George S. Pope, the engineer in charge of such investigations and the author of the bulletin, makes the following statements:

To determine with utmost accuracy the ash content and heating value of a quantity of delivered coal would require the burning of the entire quantity, and special apparatus arranged to measure the total heat liberated, or would require crushing the whole quantity, and reducing it by an elaborate scheme of successive crushings, mixings, and fractional selections to portions weighing approximately 1 gram, the minute quantity which the chemist requires for each determination. Either of these procedures is obviously impracticable if the coal is to be used for the production of heat and power.

The method actually employed is to select portions from all parts of a consignment or delivery of coal and to systematically reduce the gross sample, obtained by mixing these portions, to quantities that the chemist requires for making ash determinations or that can be burned conveniently in the calorimeter, an apparatus for determining the heating value. The gross sample should be so large that the chance admixture of pieces of slate, bone coal, pyrite, or other impurities in an otherwise representative sample will affect but slightly the final results. Increasing the size of the gross sample tends toward accuracy, but the possible increase is limited by the cost of collection and reduction. In reducing the gross sample by successive crushings and halvings or fractional selections, the object is to procure a small laboratory sample that, upon analysis, will give approximately the same results as the gross sample itself, or, in fact, the entire quantity of coal from which the gross sample was obtained.

Recognizing the importance of the method of sampling as being a definite commercial procedure and of having the method clearly set forth in the specifications to become a part of the contract, and recognizing also the desirability of insuring uniformity and similarity in the specifications used by the different branches of the Federal service for the purchase of coal, representatives of the executive departments and independent establishments of the Government held a

conference under the auspices of the Bureau of Mines in February, 1912, for the purpose of discussing these and other features of the specifications. At this conference committees were appointed to prepare specifications in accordance with the views of the members. It was recognized at the conference that in general specifications, such as were recommended, certain requirements had to be of wide application, as the specifications cover such a wide variety of conditions, not only as to character and quality of coal but as to type of furnace equipment, size of deliveries, methods of delivering, etc.

The specifications which were used for the purchase of coal on the heat-unit basis prior to the fiscal year 1912-13 were on the B. t. u. (British thermal unit) "as received" basis; that is, payment for delivered coal was directly affected by the moisture content of the sample received by the laboratory. This method was based on the assumption that the moisture in the samples collected at the time of weighing and delivery could be preserved with slight loss during the storing and subsequent working down of the gross sample to a quantity convenient for transmittal to the laboratory and in its later treatment in the laboratory. From experiments that have been made and from a large mass of data, it is known that the moisture content of coal does not remain constant, and that the moisture content reported by the laboratory may be as much as 5 to 10 per cent lower than that actually contained in excessively wet or high-moisture coal at the time of weighing.

* * * As a sample loses moisture, its B. t. u. "as received" value correspondingly rises, with the result that the price for delivered coal determined on the "as received" value is, with rare exceptions, higher than that warranted by the quality of the coal at the time of weighing. As a general statement, payment based on the "as received" B. t. u. value will be higher than warranted, unless the sampling and laboratory work can be carried on under conditions that minimize moisture loss, as under freezing temperatures.

Recognizing the uncertainty involved in taking the moisture determination in the laboratory as representative of the moisture content of the delivered coal and the consequent possibility of payment of a higher price than is warranted, the Bureau of Mines recommended to the executive departments and independent establishments of the Federal service that the heating value in the coal specifications for the fiscal year 1912-13 be on the "dry coal" basis.

In preparing these specifications the fact was recognized that the amount of moisture contained in coal produced from day to day from the same mine, or group of mines working the same bed, is largely accidental, and is a matter over which the buyer and seller have only slight control. However, in order to place a negative value on high-moisture coals and to protect the Government against the delivery of coals containing excessive amounts of moisture, the specifications require the bidders to specify the maximum moisture content in coal offered. This value becomes the standard of the contract.

If coal of uniform B. t. u. "dry coal" value is delivered on a contract, the contractor receives the advantage on any delivery in which the moisture content approaches the maximum specified, because he is paid for the weight of water contained in the coal in excess of a normal amount, whereas if the coal is very dry, containing less than the normal amount of moisture, the purchaser receives the advantage.

* * * As an example of the effect of a heavy rain on a car of coal in transit, a precipitation of 3 inches of water on a loaded 50-ton car, area of top about 360 square feet, would increase the weight of the coal 5.01 per cent, provided none of the water drained out or evaporated. It is obvious that if this coal is weighed and delivered immediately, special samples for moisture determinations should be collected and prepared at once and sent to the laboratory, as a basis for equitable adjustment of payment on account of the excessive amount of water in the coal. As the weight of the coal was increased by the excess water, there should be a corresponding decrease in the price to be paid.

If a railroad car or wagon so rained on should not be unloaded immediately after weighing and special moisture samples should not be properly collected, prepared, and sent hermetically sealed to the laboratory, it is obvious that the purchaser would pay a higher price than warranted, especially if the car or wagon stood for some time before sampling and some of the water drained out. Further, if the coal was not immediately unloaded and sampled or if the car continued in transit after weighing, then the coal at the top would soon dry; and in either case the effect of the 3-inch rainfall, as indicated by the analysis, might be only a fractional percentage of the moisture contained in the coal at the time of weighing.

The determination of the moisture of coal delivered from stock piles is often of great importance, for the proportion of moisture contained in the small sizes, which are most abundant near the center of a stock pile and which absorb the rains, and melting snows in districts of heavy snows, may be from 10 to 15 per cent higher than when stocked. It is apparent, therefore, that special moisture sample determinations are necessary for equitable adjustment of payment on amount of excessive moisture in coal which is stocked in piles exposed to the weather.

The specifications provide for the collection of "special moisture samples," if, in the opinion of the Government officials sampling it, the delivery contains moisture in excess of that guaranteed by the contractor. The "special moisture samples" are prepared in a manner to minimize moisture losses and may be taken and prepared independently of the gross samples collected for the determinations of heating value (B. t. u.), ash, and other specified data. If the analysis

of the special sample shows a moisture content in excess of the contractor's guaranty, a proportionate deduction is made from the price to be paid for the coal.

Copies of this bulletin may be obtained by addressing the Director, Bureau of Mines, Washington, D. C.

RECENT PATENTS.

The following patents relating to industrial and engineering chemistry are reported by C. L. Parker, solicitor of chemical patents, McGill Building, Washington, D. C.

1,054,735. Process for the Preparation of *Formates of Chromium, Aluminum and Iron.* Albert Wolff, Cologne, Germany. Patented March 4, 1913.

1,054,756. Process for *Preserving Wood* and Products Thereof. Carleton Ellis, Larchmont, N. Y., assignor by mesne assignments to Copper Oil Products Company, a Corporation of New York. Patented March 4, 1913.

1,054,777. *Explosive.*. Roberto Imperiali. Brescia, Italy. Patented March 4, 1913.

1,055,103. Process for Producing *Sulfonic Acids* of the Naphthalene Series. August Vagt, Leverkusen, near Cologne, Germany, assignor to Farbenfabriken vorm Friedr. Bayer & Co., Elberfeld, Germany, a Corporation of Germany. Patented March 4, 1913.

1,055,119. Alloy of *Platinum and Osmium.* Fritz Zimmerman, Newark, N. J., assignor to Baker & Company, Newark, N. J., a Corporation of New Jersey. Patented March 4, 1913.

1,055,334. Process of Making *Gas.* Wilbur G. Laird, Washington, D. C., assignor to The Improved Equipment Company, New York, N. Y., a corporation of Colorado. Patented March 11, 1913.

1,055,405. Method of Producing Compounds of *Formaldehyde* with Sugars. Richard Lauch and Fritz Quade, Berlin, Germany, assignors to Johann Abraham von Wulfing, Berlin, Germany. Patented March 11, 1913.

1,055,495. Process for Treating *Ores.* Carl Schick, Siegen, Germany. Patented March 11, 1913.

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THE PRODUCTION OF AVAILABLE POTASH FROM THE NATURAL SILICATES.*

By ALLERTON S. CUSHMAN AND GEORGE W. COGGESHALL.

The great demand which has recently arisen for an American supply of potash in available form for agriculture, has stimulated not only the search for new sources of this material, but also experiments on a large and practical scale of operation, in the attempt to develop a method of making the vast supply of potash locked up in feldspars and feldspathic rocks either directly water-soluble or sufficiently soluble in dilute acids to insure a product which shall be useful as a fertilizer. The natural silicates commercially available as sources of potash are chiefly orthoclase and leucite. Both of these minerals are potassium-aluminum silicates. The theoretical formula for orthoclase is written $K_2O.Al_2O_3.6SiO_2$, and for leucite $K_2O.Al_2O_3.4SiO_2$. The principal sodium feldspar, albite, has the theoretical formula $Na_2O.Al_2O_3.6SiO_2$. It is well known that these feldspars run into and substitute each other in various proportions so that the products from different quarries will vary widely in respect to their soda and potash contents. There is an enormous supply of feldspar in the United States, both east and west, which could be made economically possible as a source of potash supply, provided the cost of production can be made low enough to compete with the potash-holding manure salts which are at present so largely imported from Germany. Although it must be admitted that the imported salts are richer in potash than any product that can ever be made from American feldspars, it should also be remembered that the crude German manure salts contain large quantities of chloride, and sulphates of elements which are not only undesirable in the fertilizer but which may do actual harm under certain conditions. It is this fact which gives encouragement to the attempt to produce from American feldspar a straight potash fertilizer which could be used in exactly the same way that hardwood ashes have been found useful.

*Paper presented at the 8th International Congress of Applied Chemistry, New York, September, 1912.

Six general methods have been proposed for decomposing the natural silicates, in the effort to obtain water-soluble potash salts.

I. ADAPTATION OF NATURAL AGENCIES.

In the processes of Nature, the slow action of moisture and atmospheric agencies, including the action of carbonic acid gas, is known to have a decomposing or kaolinizing action upon the feldspars. Immense deposits of feldspar and granitic rocks have thus been decomposed, with the formation of large beds of kaolin and clays from which the potash has been leached into the surrounding valley. For this reason, the valleys between feldspathic and granitic hills are usually highly productive of the crops which require large amounts of potash, such as tobacco, potatoes, large fruits, berries, etc. There have been a few processes proposed, which depend principally upon the natural reactions hastened by pressure and other agencies. In 1904 Blackmore (U. S. Patent 772,206) proposed the action of carbon dioxide gas under five hundred pounds pressure upon a cream of the ground mineral, repeated intermittently for several hours, in the attempt to produce a yield of carbonate of potash. Ten years earlier the same experimenter (U. S. Patent 513,001) had proposed using lime, calcium chloride and steam pressure in an autoclave to produce chloride. In 1910 Coates (U. S. Patent 947,795) proposed the addition of bacteria for the decomposition of feldspar. In 1910 Carpenter (U. S. Patent 959,841) proposed to heat the mineral intensely and cool suddenly by plunging in water, in the effort to render the feldspar amorphous, in the hope of making it more available for plant growth. None of the above processes have as yet been shown to possess industrial possibilities.

II. WET PROCESSES OF A CHEMICAL NATURE.

Levi in 1904 (French patent 344,246 and English patent 13,875) and Piva in 1905 (French patent 351,338) proposed methods for treating leucite by means of solutions of alkali or alkali earth hydrates, generally under increased pressure. The same general method for treating feldspar was claimed by Swayze in 1907 (U. S. patent 862,676) and by Gibbs in 1909 (U. S. patent 910,662).

Also Gibbs in 1904 (U. S. patents 772,612 and 772,677) proposed a process of treatment with hydrofluosilicic acid, and subsequently with sulphuric acid,

in order to produce potassium sulphate. In 1907 Cushman was granted U. S. patent 851,922, a public patent which proposed the sludging of finely ground feldspar with water, the addition of a small amount in hydrofluoric acid and electrolyzing the mixture of wooden cells provided with wooden diaphragms. Under this process both potassium and aluminum hydrate passed through the cell diaphragm into the cathode compartment. This process, although perfectly practical, has not yet been made commercially possible owing to the high cost of hydrofluoric acid and the large amount of by-products formed in the process. None of the above processes have as yet been made commercial possibilities.

III. DRY PROCESSES OF A CHEMICAL NATURE, IN WHICH THE POTASH SALTS ARE VOLATIZED.

In processes of this nature, fluxes, and in some cases fuel, for reducing purposes are ground and mixed with the feldspar, the mixture being subsequently heated until the potash salts are volatilized and collected either in the stack dust or partially collected from the gases by passing them through or over water. Swayze in 1905 (U. S. patent 789,074) heated ground feldspar with gypsum and carbon, and proposed to collect the volatilized sulphate. Spencer and Eckel in 1909 (U. S. patent 912,266) made a cement mixed with calcareous and siliceous fluxes and green sand, a natural potash-bearing iron silicate, clinkered the mixture in a rotary cement furnace, and obtained a Portland cement, at the same time collecting the potash in the stack dust and the flue gases. In 1911 Eckel (U. S. patent 1,011,172) proposed a somewhat similar method but heated only high enough to drive off the potash salts and not high enough to clinker the mixture. Again, in 1911, Eckel (U. S. patent 1,011,173) melted a mixture of green sand, limestone and fuel, tapped off the melted iron and slag, and recovered the potash salts from the flue gases.

Some of the processes under this heading have been tried on a large scale. No great difficulty is recorded in driving off the potash in the furnaces, but obstacles were encountered in the attempt to collect the potash from the gases. As a by-product operation in the manufacture of cements, these processes may yet come to be of some industrial importance.

IV. DRY PROCESSES WHICH PROPOSE TO SEPARATE POTASH A. HYDROXIDE OR CARBONATE.

The old method of Bickel, proposed in 1856 (U. S. patent 16,111), which depended upon heating a mixture of feldspar, lime, and natural phosphate rock or guano to a bright red heat, has not as yet been proved practical or successful. The process of the Soc. Romana Solfati in 1905 (French patent 352,275), which proposes the roasting of leucite with carbonate, hydrate or nitrate of soda and lime and subsequently the passage of steam through the roasted product to produce sodium aluminate and potassium carbonate, is possible from a chemical standpoint, but the high cost of operation has not permitted the process to come into commercial use.

V. DRY PROCESSES PRODUCING THE CHLORIDE.

These processes have been most experimented with upon the mill scale of operation. In 1900 Rhodin (U. S. patent 641,406 and *J. Soc. Chem. Ind.*, 20, 439) proposed fritting feldspar with lime and salt. According to the published results, this experimenter obtained good yields although the process has not become a commercial success. In 1907 McKee (U. S. patent 869,011) suggested heating a potash-bearing material containing mica with lime, salt and carbon in order to obtain a yield of potassium chloride. Cushman in 1911 (U. S. patent 987,436) proposed mixing feldspar with lime and salts of a mineral acid capable of decomposing the silicate, giving the mixture special treatment previous to heating in a rotary furnace in order to produce the chloride. This method has been tried out on a large mill scale of operation, and the results obtained will be discussed later on in this paper.

VI. DRY PROCESSES PRODUCING SULPHATES.

In 1911 Thompson (U. S. patent 995,105) proposed heating to a bright red heat a mixture of feldspar, sodium acid sulphate and sodium chloride, and subsequently leaching out the potassium sulphate produced. This experimenter claims that potassium chloride is first formed, which is subsequently changed to the sulphate by the action of the acid sulphate. It is stated that this process has recently been tried on a commercial scale of operation. Sodium acid sulphate is a by-product that is reasonably cheap although a large quantity is not available. The lack of an abundant supply of acid sulphite is perhaps the greatest drawback to the commercializing on a large scale of this process, although it is possible that it may still become of some industrial importance. Hart, in 1911 (U. S. patent 997,761), proposed to fuse feldspar with some barium compound, such as the sulphate, together with carbon, to pulverize the cooled melt and subsequently to digest the product with sulphuric acid and thus produce in solution potash alum and a residue of barium sulphate and silica which is claimed to be useful as a paint pigment. Hart claims that some of the potash is volatilized during fusion. Since the fusion temperature is 1500° C., it is probable that a considerable portion of the potash does volatilize, and it is possible that this difficulty may interfere with the commercial success of the process. Wadman, in 1907 (U. S. patent 847,856), proposed heating lepidolite with potassium sulphate and leaching the product with sulphuric acid in order to obtain sulphates of lithium and potash.

A chronological list of the patents which have been granted for the treatment of the silicates for the production of available potash is given in Table I.

It would appear that the most promising processes for making potash available from the natural silicates on a commercial scale of operation are those which are conducted in the dry way but without actual fusion of the reacting mixture. Potash salts volatilize readily at the high temperatures necessary for the fusion of the silicates, and the collection of the volatilized potash from the stack gases has not yet been carried out economically. A considerable portion of the potash does not settle in the dust chamber, and if water sprays are used for washing the gases, the potash solutions are very dilute and the cost of evaporation becomes prohibitive. Furthermore, water sprays are found to interfere with the draft regulation, even when the use of fans is resorted to. The maintenance of artificial draft is an expensive and difficult matter, and it is very likely to interfere with the proper control of the furnace temperatures. For work on the large scale of mill operation, a continuous process must be used, avoiding fusion and with the regulation of temperature to the exact point at which appreciable quantities of potash do not volatilize. The fluxes and reacting substances must be cheap, available in large quantity, and the yields of water-soluble potash salts must be high. The process which has seemed to us to give the most promise of successful adaptation to commercial ends is that of Cushman (U. S. patent 987,436) coupled with the method of preparation of the materials before furnacing, proposed and developed by Coggeshall (U. S. patent 987,554).

TABLE I.—PROPOSED EXTRACTION PROCESSES CHRONOLOGICALLY ARRANGED.

Process.		Year.	Patentee.	Product.
IV.	Lime, $Ca_3(PO_4)_2$, red heat	1856	Bickell	Potassium hydroxide
I.	Lime, powdered $CaCl_2$, H_2O, steam	1894	Blackmore	Potassium chloride
V.	Lime, salt, heat under melting	1900	Rhodin	Potassium chloride
II.	$Ca(OH)_2$ or NaOH, pressure 16 atmospheres	1904	Levi (leucite)	Potassium silicate
II.	H_2SiF_6 and H_2SO_4	1904	Gibbs	Potassium sulphate
I.	CO_2 500 lbs. pressure repeating	1904	Blackmore	Potassium carbonate
II.	(Leucite) KOH, NaOH, steam 25 atmospheres	1905	Piva	Potassium silicate Potassium aluminate
IV.	(Leucite) alkali, carbon, CaO red heat	1905	Soc. Romana Solfati	Potassium carbonate
III.	Gypsum and carbon, fuse, volatilize	1905	Swayze	Potassium sulphate
VI.	Lepidolite, K_2SO_4, H_2SO_4	1907	Wadman	Potassium sulphate
II.	Water and HFl electrolysis	1907	Cushman	Potassium hydroxide
II.	Heat alone, then KOH solution	1907	Swayze	Potassium silicate Potassium aluminate
V.	"Containing mica" with CaO, NaCl and C	1907	McKee	Potassium chloride
II.	$Ca(OH)_2$ steam 150 lbs.	1909	Gibbs	Potassium hydroxide
III.	Green sand cement mix volatilize	1909	Spencer and Eckel	Potassium salts
I.	Bacteria action	1910	Coates	
I.	Intense heat, sudden cooling alone	1910	Carpenter	
V.	CaO, $CaCl_2$, etc., clumps, red heat	1911	Cushman	Potassium chloride
VI.	$NaHSO_4$, NaCl bright red	1911	Thompson	Potassium sulphate
VI.	Ba compound as $BaSO_4$ and C, fuse, H_2SO_4	1911	Hart	Potassium alum
III.	Cement mix but not over 900° C. with green sand volatilize	1911	Eckel	Potassium metallic Potassium sulphate
III.	Green sand, CaCO and C, melt, iron volatilizes	1911	Eckel	Potassium sulphate

This process has recently been given extensive trials on a large scale and interesting results have been obtained. The process consists essentially in powdering 100 parts of potash feldspar rock together with about 20 parts of lime and with or without 10 to 20 parts of rock salt. This powdered mixture is fed to the top of a moving drum about three feet in diameter, in a layer about half an inch deep. As soon as the layer is formed a strong solution of calcium chloride is applied from a series of small tubes. The calcium chloride at once unites with the lime, forming a so-called oxychloride cement and a large portion of the mixed powder is thereby at once formed into "clumps" or aggregates lying in a bed of surplus powder. As the drum revolves the bed is removed by a scraper to a belt that delivers the mixture to a screen which separates the clumps from the residual powder. The powder is returned by a screw conveyor and elevator to the hopper above the drum again. The clumps are about the size of peas and pass from the screen directly to a rotary kiln similar to those used in burning Portland cement. The kiln is heated by a blast of air and powdered coal in the usual manner.

The clumps pass regularly down through the increasingly heated portions of the rotating kiln and roll out at the end, practically without alteration in size and shape.

A large percentage of the total potash present in the feldspar is converted into potassium chloride during the heat treatment, and very little is volatilized. The dry clumps are of a pale yellow color outside, due to the iron in the ash of the bituminous coal used, but they are snow-white inside. The clumps are finally ground, producing a pale yellow material containing as much water-soluble K_2O as hardwood ashes, although the potash is in the form of chloride, and the product also contains considerable free lime. Up to the present time no attempt has been made on a large scale to leach out the soluble potash. The ground material is being given field tests as a straight potash fertilizer containing lime

A RESUME OF THE LARGE SCALE EXPERIMENTS.

Potash feldspars were obtained from five different localities. Eleven carloads were used in the trials, amounting to a total of 385 tons. Each carload was

ground and analyzed separately. The lowest in potash ran 6 per cent. K_2O and 3 per cent. Na_2O, the highest 11.3 per cent. K_2O and 3.1 per cent. Na_2O. The bulk of the spar ran 10 per cent. potash and 2 per cent. soda, and the results given in this paper were obtained on this 10 per cent. spar.

The lime was a high calcium quicklime, running about 90 per cent. CaO and 5.6 per cent. MgO.

The salt was rock salt from New York state and ran about 98 per cent. NaCl.

The calcium chloride was obtained from the Solvay Process Company. It was in the solid form and contained about 75 per cent. $CaCl_2$ and 25 per cent. water.

All of the above materials are available in very large quantities and at low cost. The calcium chloride is a by-product in the form of a moderately strong solution, and but a small portion is concentrated at the present time, as the chief use is for refrigerating purposes. Vast quantities are now run to waste. The solid form was used in these trials merely for convenience.

Many heats were made with mixtures of varying proportions, but the two mixtures used in the work here described were:

	Parts.		Parts.
Feldspar	100	Feldspar	100
Lime	20	Lime	20
Salt	10	Salt	20

The feldspar, lime and salt were separately crushed in gyratory crushers and rolls, and dried in a rotary drier. In continuous work the proper mixture would be made at this point by continuous weighing machines, but as a number of different mixtures were to be tried, each of the three raw materials was ground separately in Huntington mills and put into bins. This preliminary grinding of the feldspar and salt was to about 65 per cent. through a 100-mesh sieve, of the lime about 83 per cent. through the 100-mesh. The weight per cubic foot of each powder of the above fineness was then ascertained and measuring boxes were built so that the materials could be separately measured out and run together into a large mixing machine. Almost a ton was thus mixed each time. The mixture was then conveyed to a tube mill and further ground to a fineness of from 97 per cent. to 99.5 per cent. through a 100-mesh sieve, and then conveyed to the bin over the clumper and kiln.

The calcium chloride masses were broken up and thrown on a perforated grid in a large tank holding about 48 tons. Water was run in and the chloride dissolved most readily. The solution was run out when about 42 degrees Baumé into two large sump tanks, and brought to a constant strength of about 42 per cent. $CaCl_2$. This was then pumped up to an elevated tank and piped from there, through a constant-level tank, to the dropper tubes of the clumper placed in a row above the drum. This drum is 15.5 feet long and 3 feet in diameter, and is horizontal. There are 15 valved pipes, each one feeding an adjustable pipe holding 38 short dropping tubes of brass 1-16 inch internal diameter, and set 5-16 inch apart.

The finely ground mixed powder is taken from the bin by a chute, elevator and screw conveyor and distributed in a long hopper trough over the drum. It is taken from the trough by a roll device and spread evenly on the moving drum at its topmost point. The drum has a surface velocity of about 1.6 inches per second, the layer of powder advancing at this rate.

It was found that by dropping the liquid very rapidly upon the powder, the clumps could be made rapidly enough to give a full feed to the short rotary kiln when only one-third of the trough and droppers and drum is used. A clumper drum 5 feet long produces every hour almost two tons of fresh clumps and considerably over a ton and a half of burned product with the kiln used in these trials. The excess of powder passes through a screen and goes to the same elevator which lifts the original material from the bin. The amount of actual $CaCl_2$ in the fresh lime is regulated to about 20 parts to each 100 parts of faldspar in the mixture. The clumps leave the screen in rounded form and flow directly into the kiln.

The reason for the above procedure will now be explained. In the first place, calcium chloride reacts very efficiently under these conditions with the feldspar by replacing the potassium with calcium, thus forming calcium silicate and potassium chloride. Anhydrous calcium chloride is expensive to produce and it is impracticable to grind it into a mixture on a large scale on account of the rapid absorption of moisture. Even if such a dry mixture could easily be made, its use would present certain disadvantages.

When a reaction between an ore and solid fluxes is produced by heating up to the fusing temperature, the reaction takes place on the surface of the particles alone and only at the points where the ore is in actual contact with the flux particles. Finer grinding will produce a larger surface area and thus a greater number of actual contact points, leading to a larger yield. There is, however, a degree of fineness beyond which it is not wise to go, on account of the cost of extremely fine grinding.

Another factor in the problem is brought out by the following experiments: A batch if ore and the theoretical amount of solid flux were ground together to just pass a 50-mesh sieve. This powder, when subjected to a certain heat treatment, gave a reaction yield of about 35 per cent. of the theoretical. The mixture was then ground to just pass a 100-mesh sieve and given the same heat treatment. A reaction yield was obtained of about 65 per cent. of the theoretical. The mixture was then ground to pass a 200-mesh sieve and again reheated as before. A smaller yield was obtained than when the mate-

rial just passed the 100-mesh, although the particles were undoubtedly only half the average diameter with about four times the surface area and should therefore have had far more points of contact. Upon weighing equal volumes of the 50-mesh, 100-mesh and 200-mesh powders, it was found that the latter contained far less material and it became apparent that the 200-mesh powder consisted for over 54 per cent. of its volume simply of voids. Such finely ground powders are well known to "surge," that is, to show the tendency to flow like water through orifices in a manner resembling fountains. Material ground as fine as this is the cause of much trouble at spout slides and conveyors. Each particle of a material of this extreme fineness is undoubtedly surrounded by a film of air, the actual contact with the surfaces is lessened and friction almost eliminated. When allowed to flow into a bin, such a powder assumes an almost horizontal surface: there is practically no angle of repose. Unquestionably the lessened contact caused the low yields in the finely ground mixtures. Some of the fined materials were briquetted and the subsequent heat yielded about 85 per cent. of the theoretical. Briquetting is, however, expensive and usually necessitates the addition of a binding agent foreign to the reaction.

As a result of these investigations, the method was developed for aggregating fine powders by dropping a suitable liquid upon an excess of the powder in such a way as to cause a temporary bond to form, thus practically eliminating the air films or voids around the individual particles and permitting actual surface contact. Under these conditions, with the same ore and flux used in the experiments described above, the same heat treatment yielded within 3 per cent. of the theoretical quantity present. This method of aggregating finely powdered materials previous to furnacing has already been used in several different ways. For example, in an ore mixture in which the flux material is an alkaline carbonate, such as sodium or potassium, which form crystalline salts containing water of crystallization, if the carbonate is used in the partially anhydrous condition and ground with the ore, water alone dropped upon the mix in the manner described formed at once a crystalline carbonate which binds the particles of ore and flux into separate clumps, which are hard enough to withstand screening, while the air films are practically eliminated. Using such a mixture and process as this, a practically theoretical yield was obtained, although the flux was used only in the exact molecular proportion called for by the reaction.

By this clumping process a very intimate contact of reaction of surfaces is readily obtained at a low cost. The quantity of flux necessary to complete the reaction is greatly reduced, the duration and temperature of the heat treatment is lessened and working with rotary kilns dusting and stack losses are almost entirely eliminated. The clumps are beautifully adapted to the feed mechanism of rotary kilns, as they flow easily, do not dust, and take the heat more evenly than fine powders. Now that the temperature conditions in rotary kilns can be accurately controlled, it would seem that many chemical and metallurgical reactions which are now performed by intermittent processes and with low yields could be much more economically carried out in continuous rotary kilns, taking advantage of this new method of forming aggregates previous to furnacing.

In the application of this method to the treatment of feldspathic rock, advantage was taken of the fact that a solution of calcium chloride acts upon dehydrated lime to form the oxychloride which is a strong cementing compound. It was found that the formation of calcium oxychloride gave a sufficiently strong bond to enable the aggregates to withstand the operation of screening and the burden in the kiln.

The theoretical quantity of calcium chloride flux required depends upon the total quantity of K_2O and Na_2O present in the mix, as it is evident that the soda must also be liberated in proportion to its content. The feldspar ore used ran 10 per cent. K_2O and 2 per cent. Na_2O, which required theoretically 15.5 parts of calcic chloride. In all our trials some slight excess of calcium chloride has been used. The strength of the solution and the method of treatment has been such that about 20 parts of actual calcium chloride are present in the fresh clumps to every 100 parts of feldspar. The 20 parts of lime used is for the purpose of forming the aggregates, and this lime remains practically unchanged in the finished product. The presence of lime in a potash fertilizer will be found advantageous to most soils, and it is generally admitted that lime increases the manurial value of a fertilizer. If the object were to leach out the soluble potash salts from the product, a much smaller amount of lime could be used without interfering with the formation of hard clumps. The salt is added because it has been found to aid the heat reaction, probably mechanically as will be explained later on. The fresh clumps contain from 16 to 20 per cent. of moisture, which, is, of course, evaporated in the upper part of the kiln.

The rotary kiln used in these trials was one of the old bottle-shaped cement kilns with a total length of slightly over fifty-five feet, the upper twenty feet having a diameter of 4 feet clear inside the firebrick lining, the lower portion widening out to nearly 6 feet inside diameter. The pitch was ⅞-inch per foot and the most suitable speed was found to be one revolution in about 2½ minutes.

The conditions of the heat treatment are very important. The kiln used was too short to yield the best results, and after the preliminary experiments changes were made which caused the material to take about 1½ hours to pass through the length of the kiln. The temperature of the gases issuing from the upper end of the kiln were read continually with

a thermocouple pyrometer fitted with a 15-foot fire end and temperatures were also taken from time to time at the firing platform. A furnace wall temperature of about 1370° C. is required for efficient burning of powder bituminous coal. This is, however, much too high a temperature for potash work in a rotary kiln. This difficulty called for careful experimental investigations and adjustments of the heat treatment before the proper yields could be obtained. If a longer kiln had been available, there is every reason to believe that a more efficient use of the heat could have been obtained. The coal used was a fairly high volatile bituminous coal. It was ground to about 94 per cent. through a 100-mesh sieve and blown into the furnace under an air pressure of about ten pounds per square inch.

During the progress of the clumps down the kiln the following reactions probably take place: At the entrance to the kiln the water begins to evaporate. As the hotter zone is approached, the temperature rises high enough to melt calcium chloride and salt. Whether the calcium chloride is free to melt is not known to us, as the exact composition of the oxychloride compound formed has not yet been determined. The results of our work seem to prove that the reacting chlorine is more readily evolved from th oxychloride compound than it is from calcium chloride alone. The melting of the salt, however, continues the bond of the reacting particles, causing them to thoroughly "wet" each other, and from this point on the attack on the silicate proceeds rapidly. During the heating usually from 1 to 2 per cent. of Na_2O is volatilized.

When operating with no salt present, the yield of soluble potassium chloride was 47.5 per cent. of that originally present in the feldspar. On adding to the mixture 10 parts of salt to each 100 parts of spar, a test heat yielded 64 per cent., but of this 9 per cent. was lost by volatilization, giving a yield of 55 per cent. net in the final product. On adding 20 parts of salt to the mixture the yield grows to 69.2 per cent. with no volatilization and to 75 per cent. under heat conditions which caused a volatilization of 7 per cent., leaving a net yield of 68 per cent. of that originally present. In the case of clumps made from a mixture of 100 parts of feldspar containing 10 per cent. K_2O and 2 per cent. Na_2O, 20 parts of lime, 20 parts of salt and 20 parts of calcium chloride, the theoretical composition if no volatilization loss takes place is shown compared with the actual results obtained in the following table:

	Theory. Pct.	Analysis. Pct.	
Total K_2O	6.25	5.8	
Water-soluble K_2O	...	4.2	Equals 6.65% KCl
Loss of K_2O	...	0.5	As KCl already formed
Total Na_2O	7.62	7.1	0.52% made into NaCl
Water-soluble Na_2O	6.37	5.1	Showing 1.79% vaporized as NaCl, or 26% of that present

This product contained 12.25 per cent. of free lime and total lime by analysis 15.5 per cent. There was also in this sample about 5 per cent. of free unchanged calcic chloride. The amount of calcic chloride in the various runs made up to the present time have been reduced gradually to about per cent., and it is felt that in the future better conditions of heat treatment will make complete use of the calcic chloride and at the same time raise the yields of soluble potash. In later runs in which only 10 parts of salt were present in the mix, the theoretical and actual analysis of the product was as follows:

	Theory. Pct.	Analysis. Pct.	
Total K_2O	6.66	5.62	
Water-soluble K_2O	...	4.5	Equals 7.12% KCl
Vaporization loss of soluble K_2O	...	1.04	As KCl already formed
K_2O insoluble in water	...	1.12	
Total Na_2O	4.15	...	
Water-soluble Na_2O	...	3.7	Showing 0.45% vaporized as NaCl, or 11% of that present

This product contained 12:25 per cent. of free lime, the total potash rendered soluble was 5.54 per cent. of the product or 83.2 per cent. of the total quantity present, but as 15.6 per cent. had been volatilized the net yield in the product amounted to 67.6 per cent.

The material which was later made continuously according to the process described above carries 4.5 per cent. of water-soluble K_2O in the form of 7.12 per cent. potassium chloride and in addition to this the material carries only 1.12 per cent. K_2O insoluble in water. It is well known that a 2 per cent. citric acid solution will extract, when used according to the Wagner method, somewhat more K_2O than can be made directly water-soluble. This fact is of considerable interest when the product is to be used directly as a potash fertilizer.

CONCLUSION.

It is believed that under better conditions of heat treatment which can be obtained with longer kilns and with a somewhat different arrangement of the combustion chamber, slightly better yields than those reported can be obtained. It should be remembered that the kiln used in these experimental trials was originally designed for burning cement, but this type of kiln has long been superseded by improved forms. In order to get the proper heat treatment in the middle of the kiln to complete the reaction, it was necessary to have the upper part too hot. This condition will not maintain in a properly designed kiln. It is also believed that the use of oil as fuel would have allowed an easier regulation of the heat treatment but the trials so far undertaken have been made under conditions which were found available at the time.

The subject of the costs of this process and of the product cannot be gone into in detail at this time, but a few general statements may be made. The production of water-soluble potash in feldspathic rock is essentially a low-grade proposition, and the com-

mercial success of such a process depends upon the low cost of the various operations. The manufacture of a straight potash fertilizer containing as valuable ingredients only potash and lime, must be carried out on a very large scale and by the most modern methods of continuous operation. With regard to the clumping process, the trials have shown that this operation can be practically carried out as a continuous process and at an exceedingly low charge per ton of product.

The process may be directly compared with that of the manufacture of Portland cement. It is a little easier to grind feldspar and lime than the shales and limestones used in cement manufacture. Drying will cost no more. Chemical control of the raw mixes will not be more expensive and perhaps much less. Clumping, as has been shown, adds a very small charge to the expense of treatment. The cost of furnacing the feldspar mix will be less than similar charges in the cement industry, as the temperatures required are much lower and less coal is consumed. The product from the potash kiln is comparatively soft and pulverizes easily in hammer mills, while the charges on the cement industry for grinding clinker is an important item. Again, the softer potash product merely requires to be ground fine enough for use as a fertilizer, whereas cement clinker must be ground very fine and costs rise rapidly with increasing fineness. Repair bills in the case of feldspar treatment should be much smaller than in cement manufacture. The charge for raw materials is somewhat larger than in the case of cement, but this is more than met by the smaller costs of operation.

The potash fertilizer as now produced should be the equal in fertilizing value of the ordinary grades of hardwood ashes. The product carries practically the same content of water-soluble potash and a considerable percentage of free lime. There is every reason to believe that if the process becomes an industry the yields of water-soluble potash can be considerably improved. The material yielded is not a fused product, it is friable as an ash and it has the physical texture to make it a valuable aid to soil structure. The success of the product must, of course, depend upon the results obtained under test conditions in its experimental use as a fertilizer. If results are obtained which are as good or better than those which usually attend the proper use of high-grade wood ashes, it is believed that there should be no reason why this product cannot be successfully produced and introduced, especially in those parts of the country where potash foldspars, fuel and shipping facilities are available.

The results obtained on a number of experimental trials on a mill scale of operation show that it is possible to economically manufacture a potash fertilizer containing free lime from feldspar and for a sufficiently low cost to make worthy of consideration an industry based upon the method described.

FELDSPAR PRODUCTION IN UNITED STATES IN 1912.

The production of feldspar in the United States in 1912, according to Frank J. Katz, in an advance chapter on feldspar and quartz from "Mineral Resources" for 1912, just issued by the United States Geological Survey, was 86,572 short tons, valued at $520,562, a decrease from 1911 of 6,128 short tons in quantity and of $58,446 in value. The production of crude spar was 26,462 short tons, valued at $89,001, and of ground spar 60,110 short tons, valued at $431,561. Of the total output, 1,750 short tons, valued at $17,102, was used for abrasives, and approximately 12,500 short tons, valued at $37,500, for roofing, concrete surfacing, and poultry grit. The use of feldspar of the lower grades for poultry grit, roof surfacing, and surfacing concrete work seems to be on the increase, and in 1912 small quantities were sold for experimental work on the extraction of potash.

New York led in 1912 in quantity of feldspar produced, with 22,192 short tons, valued at $101,525; Maine was second, with 19,091 tons, valued at $173,076; and Connecticut third, with 19,075 tons, valued at $94,097. Other States reporting a production of feldspar were Maryland, Pennsylvania, California, Minnesota, North Carolina, Vermont, and Virginia.

The principal use of feldspar is in the manufacture of poetry, enamel ware, enamel brick and tile, and electrical ware. Of these applications the most important is its use in the body and glaze of the various grades of pottery and vitrified sanitary ware, in which it constitutes from 10 to 35 per cent. Its value in pottery is that it melts at a lower point than the other ingredients and serves as a flux, binding the clay and quartz particles together. In glazes the percentage of feldspar used is higher than in the body and runs from 30 to 50 per cent. Other uses of feldspar, which do not require the high grade demanded by the pottery trade, are in the manufacture of emery and corundum wheels, where it serves as a binder; in the manufacture of opalescent glass; as a poultry grit; as a constituent of roofing material; and for surfacing concrete work. Small quantities of the purest grades of potash feldspar are used in the manufacture of artificial teeth. For this purpose it brings the highest prices—from $6 to $8 a barrel of 350 pounds. It is also used in the manufacture of scouring soaps and window wash. As a potash-bearing fertilizer ground feldspar has been used, but with results of doubtful value. Attempts are being made to extract from feldspar its content of potash. Experiments along this line have not yet developed a commercial process, but it is to be hoped that some of the efforts will be successful as the available supply of the raw material is practically inexhaustible.

METALLURGY.

THE MICRO-STRUCTURE OF METALS.

(Illustrated from photographs by the author.)

By H. B. PULSIFER.

Thanks to the efforts of investigators and scientific instrument makers the structural study of metals is rapidly assuming a position equally important with their chemical and physical testing.

Plenty of manufacturers and consumers of the metals persist in happily ignoring the composition or properties of the material which they daily handle, but with others the laboratory is a necessary accessory and

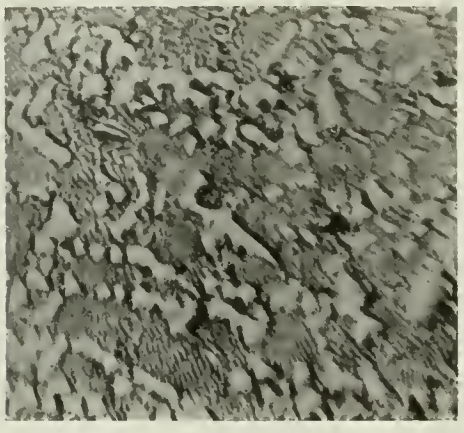


Fig. 1.—Sn-Cd Eutectic, Relief Polished, x 66.

turned to pronounced advantage. In the same way the comparatively new science of Metallography appears useless to many yet of the utmost importance to those who need and can master its subtleties.

For its own scientific and educational interest the technical schools are everywhere teaching the subject while the manufacturers are more and more requiring microscopic work done and calling for young men trained in the work.

The experience here recorded and the illustrations are from the work with the students taking metallurgy at Armour Institute during the two most recent school years. The subject is brought in as one of the topics and methods of attack throughout the lectures and laboratory work. The author's photographs, as well as the illustrations in standard texts, serve in the class room and in the laboratory each student is required to grind, polish and etch a specimen. The sample properly prepared, the student spends an afternoon with the photographing microscope. It is part of the work to get acquainted with the instrument, to try different magnifications, to measure the exact magnification and finally to expose and develop the plate.

Although the experience is only too limited, results are effective. One understands this after hearing a junior and senior discussing a print.

We have found that there is no particular advantage in preparing too small specimens. Quarter-inch sections cut from the bar, either round, square or rectangular, so as to give a length of a little over an inch

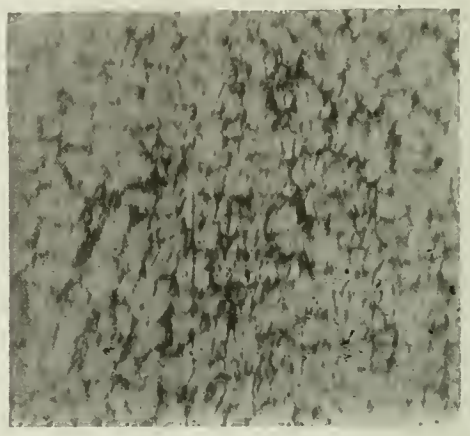


Fig. 2.—Cast Aluminum, x166, Etched with dil. NaOH.

grind easily and are handy on the stage. Surfaces as small as quarter or half inch squares polish quicker but tend to be slightly rounded and are inconvenient on the stage. A slightly rounded or tipped surface gives an unequally lighted surface with small magnifica-

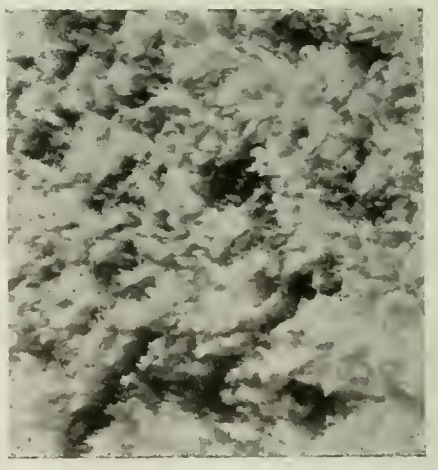


Fig. 3.—Iron Sulphide, x 166, Relief Polished.

tions and is wholly useless for more than 500 diameters.

The rectangular or round tablet first has its edges and corners rounded off with the file; it is then put on the emery wheel with plenty of water and made as smooth as possible. This accomplished, it is further smoothed on a canvas wheel with wet emery dust. As

soon as a uniformly fine surface, free from big scratches, is obtained the specimen is put on tripoli. This intermediate grinding is most important; if it is not adequately done any further work with fine polishing is wasted. The test is to use each grade of powder until it has reached its limit of smoothing effect. After tripoli on canvas jewelers' rouge on soft felt is used. For hard materials this usually furnishes a highly polished and scratchless surface which is now ready to be etched. On the other hand, with soft substances, most of this preliminary work must be carefully and quickly done and the real surfacing done with light pressure and the finest silver polish on wet chamois stretched over a board.

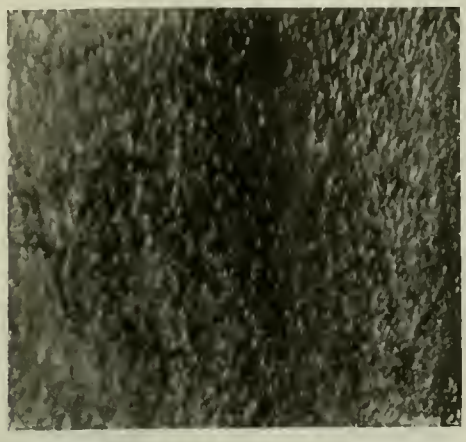


Fig. 4.—Cast Tin, x 165, Etched with Ammonium Persulphate.

Fig. 1 shows a soft tin-cadmium eutectic which has been merely polished; it was not necessary to etch it at all. It did, however, require several hours' work on the chamois and then some selection to find a spot absolutely free from scratches. In Fig. 2 we have not been as fortunate. This is a specimen of cast aluminum barely attacked by dilute caustic soda. The structure of the material is abundantly perceptible, but the mechanical treatment is also evidenced by the numberless scratch lines.

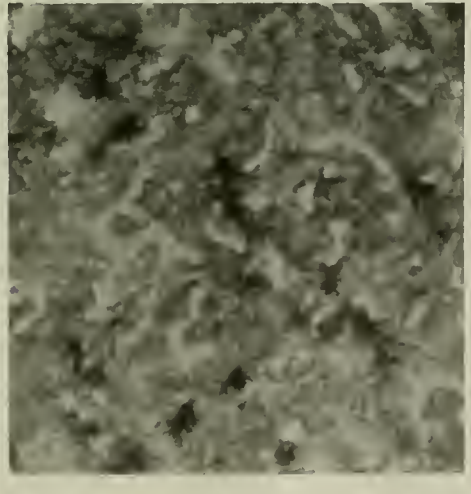


Fig. 5.—Gray Cast Iron, x 166.

For commercial work it may be enough to quickly smooth off a little area, etch and examine it, but for scientific and educational purposes it is essential to obtain a large and representative area without a vestige of furrows. Fig. 3 is a piece of iron sulphide merely relief polished.

Until the routine is fully established every step in the preparation and examination of the specimen requires much skill. Several of the specimens whose photographs are here reproduced were originally prepared by students, but in nearly all cases a final dressing by a more experienced hand became necessary to make them presentable. At the Institute we have facilities for both power and hand polishing; the combination of roughing on the wheel and finishing on the board has given the best results.

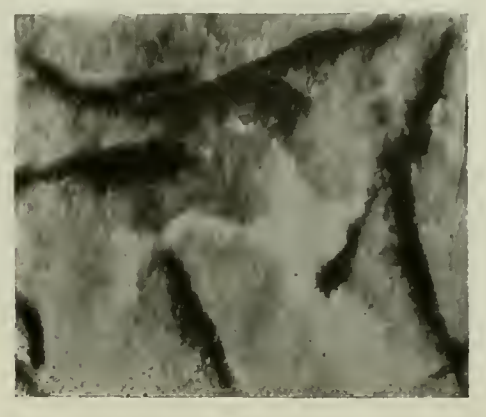


Fig. 6.—Gray Cast Iron, x 140.

As to the matter of etching there is again demanded much care and experience. Picric acid in alcohol, and nitric acid in alcohol, are excellent for many irons and steels. Numberless reagents are at hand for the special cases of either etching or coloring. The problem is to just outline the shape of the crystals or to attack one or more constituents gently and within a convenient time. Picric or nitric acid in alcohol gives about the right attack in some twenty or thirty seconds on pig and cast irons and on most soft steel. Quenched and hardened special steels may be acted on nicely with copper sulphate solution or sulphurous acid. Ammonium persulphate attacks tin and copper in just the right manner.

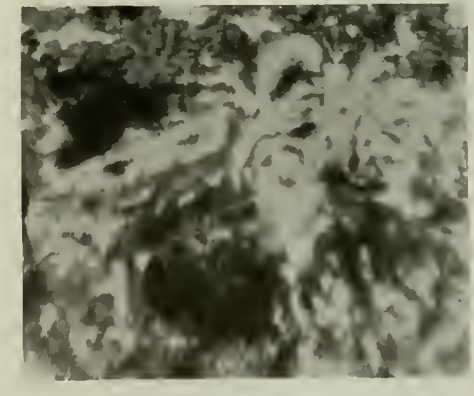


Fig. 7.—Cast Iron, x 45, Edge of Ingot.

For this sort of work it is of course necessary to have a microscope with the proper attachments for illumination, visual observation and exposing a plate. One of the latest models of Leitz-Wetzlar inverted objective, horizontal bellows, is available at the Institute. This machine readily allows of magnifications with the present equipment up to 1,500 diam-

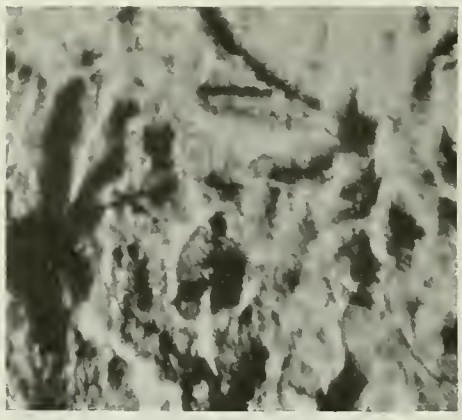


Fig. 8.—Cast Iron, x 140, Interior of Ingot.

eters. Current is convenient for the arc illumination and a dark room for changing and developing plates. The greatest difficulty which has presented itself has been the constant and insiduous, often violent, jarring. The laboratories are on the fourth floor of the main building, with a gymnasium above, traffic streets on two sides, and a four-track railroad contiguous on another side. Of course all short exposures are taken between trains, and for long ones the shutter was closed while the train passed. Some of the ex-

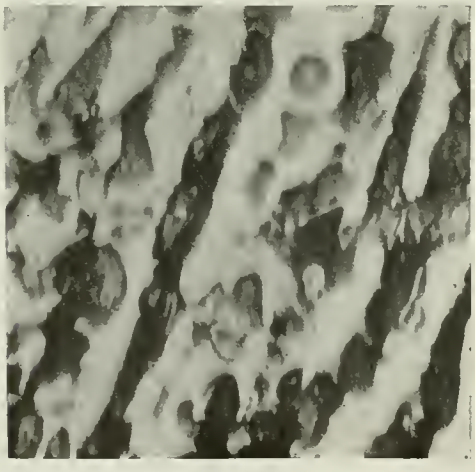


Fig. 9.—White Cast Iron, x 266.

posures were for two to three seconds, many of them for about forty-five seconds, and a few for as long as seven minutes. This is of course a matter of light intensity and the ray filter. As yet there has been little choice as to which is the better.

We have at present under way the construction of a shock-and-jar-proof cradle which it is hoped will allow of long exposures under absolute quiet. The question of jarring did not appear so serious at first nor is it so important with low magnifications; but with developing practice and larger magnifications with extended bellows it is of the utmost moment.

Quite naturally most of our work has also been to study normal and more characteristic structures rather than to look for special conditions, or fine, or abnormal features. Iron and steel has received the most attention.

In studying the various sorts of iron the use of the microscope is limited only by the ability of the observer. With a few minutes' work it allows a man to look into his material and establish a permanent record of what is to be seen. All the metals are crystalline aggregates and more or less easily resolvable into their structural units. The carbide, pearlite, graphite and ferrite in ordinary irons is easily visible at low powers and as a matter of fact tells quite as much about the material as its chemical analysis or testing machine figures.

Fig. 5 is an ordinary, close-grained, rather hard and brittle cast iron. The white carbide speaks for

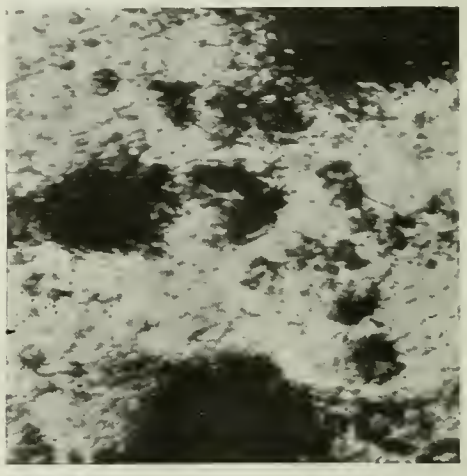


Fig. 10.—Malleable Cast Iron, x 266.

its hardness and the small spots of graphite tell of its close grain. Fig. 6 is of a slowly cooled ingot with much coarser grain. Fig. 7 is from near the edge of an ingot to show the abundance of carbide which separated near the surface as compared with the slight carbide and softer structure developed within the ingot as seen in Fig. 8. Under higher powers, which, unfortunately, we have no illustrations of, this carbide structure is broken up into a beautiful eutectic network, the pearlite is far better resolved and patches of iron and manganese sulphide can be plainly seen.

Our technical literature is at the present moment rapidly demonstrating the usefulness of this structural study of the iron series. Not alone as telling of actual condition but revealing past history and adaptability for specific purposes is delineated as one looks into the vitals of the substance. Cast, and white, and malleable iron afford concepts to all who know of them, but real acquaintance begins only with the microscopical greeting. Fig. 9 is of a little patch of clean white iron in a small casting; this bit of

white iron is wholly surrounded with good gray iron. It is from one of those pieces recently so puzzling to foundrymen, but which phenomenon Thomas D. West has so admirably cleared up and made producable at will. Fig. 10 is a bit of wholly converted malleable iron; the graphitic temper carbon is in patches of varying size and the white, more or less granular ferrite, is plainly separated into individual crystals by fine black lines. Every gradation in the change from white to malleable iron can be followed with the microscope; one can determine the influence of conditions and other constituents both on the rate of change and the final condition. The insight gained in this way is vastly more startling and clarifying than anything before available.

Now, as we come to the alloys known as steel, a stupendous field of unlimited diversity and unknown possibilities presents itself.

The annealed, low-carbon steels all show varying amounts of ferrite, characteristically present in units or crystals, the white portions of Figs. 10, 11, 12 and 13. Under low powers ferrite is commonly silvery white and uniform, rather granular under the highest powers. If the steel is properly annealed the relative area of the white portion diminishes from entire white in carbon-free iron to none, or the entire granular pearlite constituent, in steels of some .7 to .8 per cent carbon.

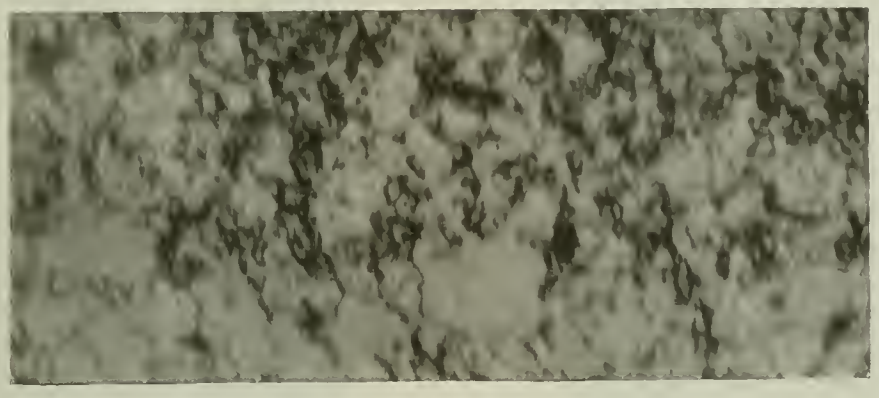


Fig. 11.—Nickel Steel, x 1000, 3.5% Ni, .2% Carbon.

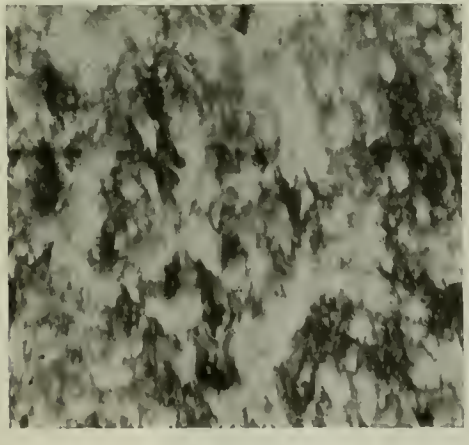


Fig. 12.—.47% Carbon Steel, x 140.

The quenched and hardened steels have strongly characteristic aspects. Austenite and martensite are found in the higher carbon series, while with lower carbon martensite and troostite are equally in evidence. Fig. 14 is a 1.00% carbon steel quenched from 1,000° C. in iced brine; the carbon is too low for much development of austenite, martensite being chiefly in evidence. Fig. 15 is all martensite as found in a .47 steel quenched in brine, the magnification is 1,000 diameters. Fig. 16 shows more troostite as the steel is .71% carbon and quenched from only 830° C. in ordinary water; the magnification is 500 diameters. The quenched steels form an extremely small bulk of the commercial materials, but for certain purposes their structure and texture is extremely important.

The sorbitic and pearlitic steels form the great bulk of commercial materials. Here we have the combination of strength, toughness and workability; also the finest and most intimate structures. These steels are the most difficult to get prints of. Under low magnification no satisfaction can be gained and with high power we get difficult manipulation and hazy outlines. Fig. 18 is our .71 carbon steel which has been hardened and then reheated, or drawn, to 400° C. The troostitic structure has nearly all faded into the dark groundmass of sorbite. Further heating or full annealing will develop the full pearlitic

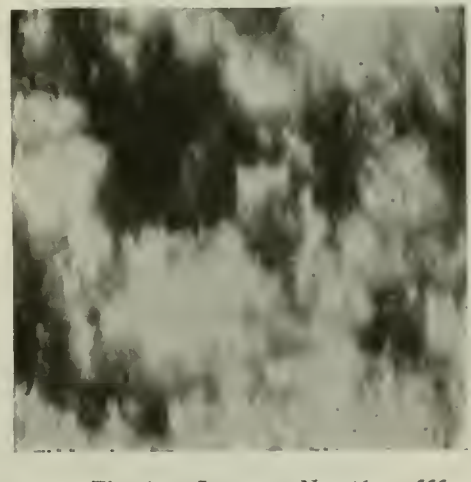


Fig. 13.—Same as No. 11, x 666.

structure which composes the field seen in Fig. 22, the same steel magnified to 1,500 diameters and largely pearlite, a few spots of ferrite have evidently segregated. The transitions from troostite, through sorbite, and into pearlite and even to granular ferrite are rather difficult to distinguish in many cases.

Possibly the finest method to become acquainted

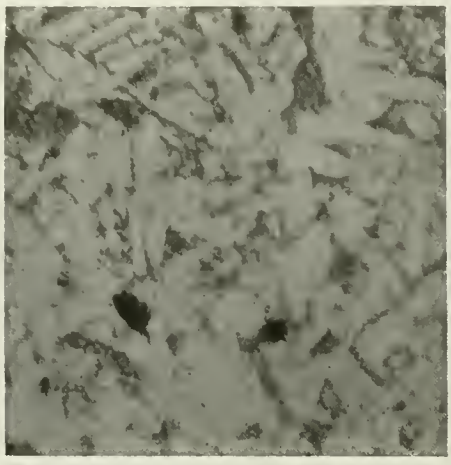


Fig. 14.—.24% Carbon, x 265, Drop-forged.

with all these transitions is to heat one end of a steel bar to a high temperature in some furnace, the other end, meanwhile, remaining cool; on quenching the bar all gradations will be found. This is known as Metcalf's experiment and for the benefit of the students is done each year by one or more students.

After the steel bar has been nicked all around at short intervals it is most thoroughly annealed from

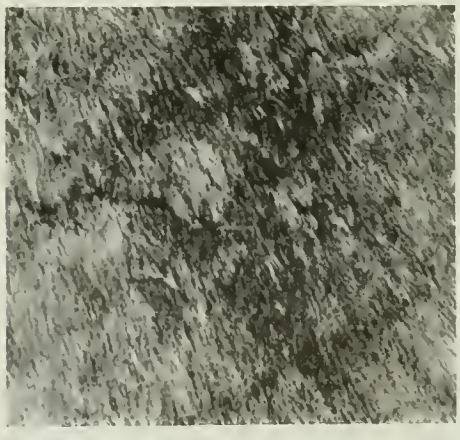


Fig. 15.—1.00% Carbon, x 166, Quenched from 1000° in Brine.

about its hardening point. The more slowly the cooling from this temperature the better will be the development of lamellar pearlite, such as is plainly shown in Fig. 19. The cold bar then has one end wrapped in a wet cloth while the other end is thrust into a gas furnace and heated as hot as possible. Meanwhile a bath of iced brine has been made ready to receive the bar the instant the hot end is taken from the furnace. The quenched bar is then broken at the nicks. The gross structure is observed at the fractured points and sections may be prepared to display the structural change.

Pearlitic structures do not seem to be as difficult to resolve as the sorbitic ones. Fig. 19 is an annealed 1.00% carbon steel, largely granular pearlite and free carbide in slight excess; most of our views show

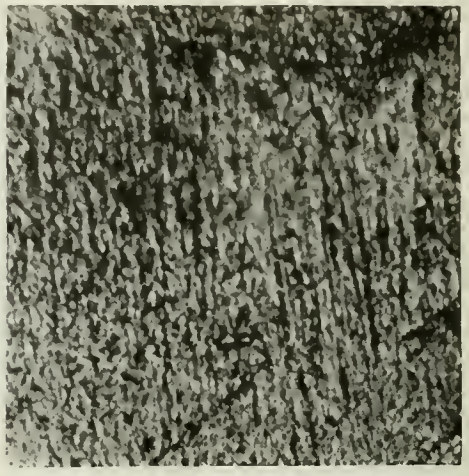


Fig. 16.—.47% Carbon Steel, x 1000, Quenched in Iced Brine.

granular instead of lamellar pearlite for all the samples had been only briefly heated and rather quickly cooled. Fig. 20 again shows granular pearlite within the large cleavage areas caused by overheating. This appearance is characteristic of steel which has been heated too hot. The sample has not yet been actually

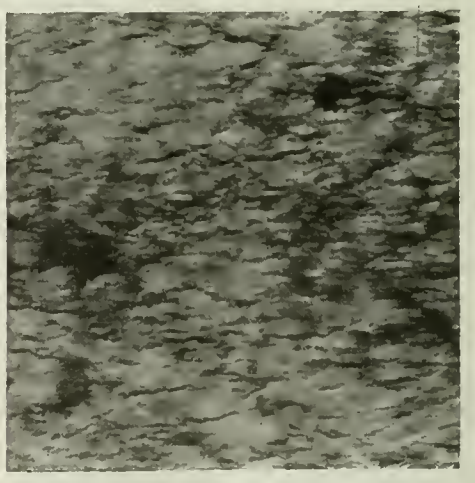


Fig. 17.—.71% Carbon Steel, x 500, Quenched from 830° in Water.

burned for no ruptures nor oxide formation resulted.

In studying steels defects are everywhere plain to be seen. Up to the present the Institute work has been rather to find and know the normal condition; accordingly in practically all the illustrations imperfections have been avoided. In actual samples blowholes, fissures, slag inclusions, specks of oxide and sulphide or unknown inclusions are constantly present to distinguish the material. Besides knowing the

Fig. 18.—.71% Carbon Steel, x 666, Hardened from 830°, Drawn to 400 C.

main constitution of the material these other matters are of vital importance to the industries. Segregations, welds and strain effects stand forth nakedly. Is the piece annealed, overheated, or has it been heat

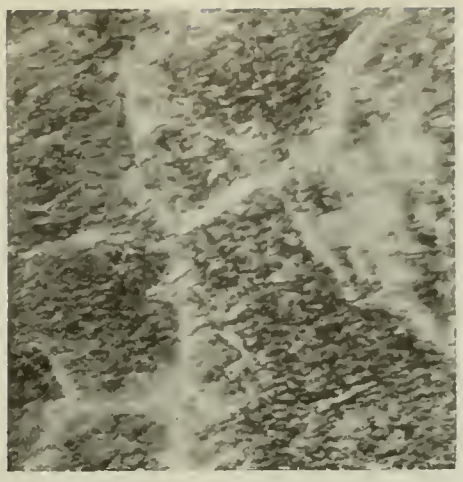


Fig. 20.—.87% Carbon Steel, x 333, Overheated.

treated? What is its hardness due to? What makes it strong? In short, are its good qualities even yet developed? To these and divers other pertinent questions metallography has an every-ready answer.

Fig. 19.—1.00% Carbon Steel, x 666, Annealed.

Fig. 21.—High-Speed Steel Quenched at Too High Temperature, x 265.

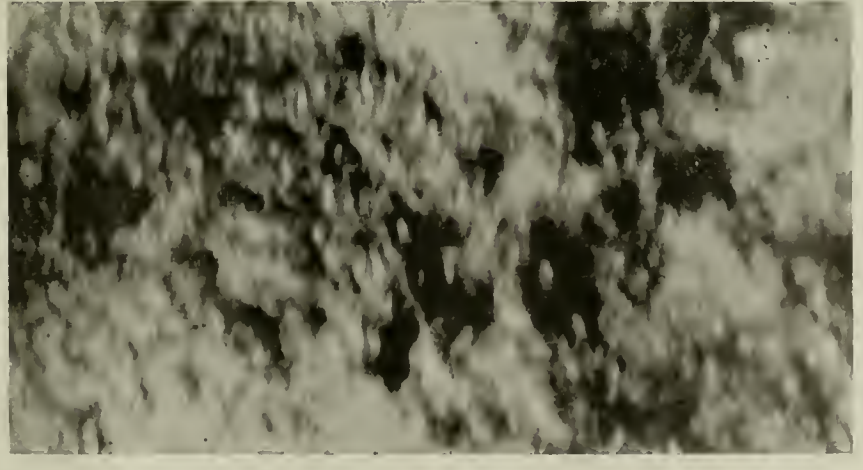


Fig. 22.—.71% Carbon Steel, Annealed, x 1000.

POTTERY PRODUCTION AND IMPORTATIONS IN 1912.

Last year, according to figures compiled by Jefferson Middleton, of the United States Geological Survey, pottery to the value of $46,059,694 was consumed in the United States. Of this sum the domestic product was valued at $36,504,164 and the imported product at $9,555,530. The output of pottery for the United States in 1912 showed an increase in value of $1,985,604 over that for 1911. Every product except stoneware and yellow and Rockingham ware participated in the increase. The variety showing the largest absolute gain was sanitary ware, which increased $870,797, and the largest proportional gain was in porcelain electrical supplies, which increased $695,215. The value of white ware, including china but excluding sanitary ware and porcelain electrical supplies, was $17,006,736 in 1912, compared with $16,424,236 in 1911. China ware showed an increase of $119,320, the value reported for 1912 being the highest ever recorded.

Ohio continued to be the leading pottery-producing State of the Union, reporting wares valued at $15,508,735, or 42.49 per cent of the total, an increase of $733,470. Ohio's principal pottery product is white ware, which represents general household wares. New Jersey was the second largest pottery-producing State, the value of its product in 1912 being $8,935,920, an increase of $533,979. The principal pottery product of the State is sanitary ware. West Virginia was third in 1912, with ware valued at $3,365,166, or $484,964 more than the value of the output in 1911. New York, Pennsylvania, Indiana and Illinois were fourth, fifth, sixth and seventh, respectively, in the value of output in 1912."

According to Mr. Middleton's report, which has been issued as an advance chapter from "Mineral Resources" for 1912, the pottery industry was in a high state of development during the year and the value of the pottery products marketed was the largest in the history of the industry. This was due partly to the general prosperity enjoyed by the country at large, but more especially to the steady improvement in the wares themselves in body, design, and decoration. American pottery is gaining a stronger hold on the market, becoming more popular every year. Many if not most of the best hotels and clubs in the country are now using large quantities of domestic china.

Raw cotton from Africa and Asia imported into England and re-exported to the United States during January-April weighed 58 million pounds.

The aggregate German imports of false flax, oil radish and hedge mustard seeds amounted to 2,681 tons in 1912, and constituted a small item in a total importation of 1,497,922 tons of vegetable oil-making materials.

THE DETERMINATION OF OXYGEN IN IRON AND STEEL BY REDUCTION IN AN ELECTRIC VACUUM FURNACE.*

By WM. H. WALKER AND WALTER A. PATRICK.

At the fifth meeting of this Congress, held in Berlin in 1903, F. Lurman presented a paper on the determination of oxygen in iron and steel in which he pointed out the necessity of a new method which would measure the total oxygen in the sample, and especially that portion which is combined with manganese, aluminium, silicon, and the other oxides not reducible with hydrogen. Since that time no advance has been made in this important field of metallurgical work.

The important role which the oxides of iron and the other metals play in determining the physical and chemical properties of iron and steel was first clearly brought out by Prof. Ledebur in 1882. At this time Ledebur proposed the analytical method for determining oxygen which bears his name and which is based upon the reduction of the oxide at a red heat by hydrogen, and weighing the water thus formed. Owing to the fact that at a high temperature hydrogen reduces only the oxides of iron, leaving unattacked to a large extent the oxides of manganese, aluminium, silicon, titanium, etc., it is obvious that the method is not a satisfactory one, although up to the present the only one available for the purpose.

Other methods have been proposed for determining the oxygen in iron and steel based upon the solution of the constituents not oxides. As examples, may be mentioned the method of dissolving the sample in ethereal solutions of iodine and bromine; or that based upon the volatilization of the iron in a stream of chlorine gas at a high temperature; but none of these methods has proven of any value.

Although the detrimental effect of combined oxygen in iron and steel has been known since the time of Ledebur's first paper, it is only within the last few years that the full significance of these effects has been appreciated. That iron oxide can exist in iron and steel in more than one form seems certain, and that the oxides of the different metals associated with the iron should have characteristic effects is surely to be expected. But in the absence of any satisfactory analytical method for determining the oxide present, the relation between cause and effect has been of necessity a most imperfect one. It is hoped that the method of determining oxygen now to be described will be an aid in establishing the connection between the oxygen content and the physical and chemical properties of iron and steel.

In the now well known reaction wherein the oxides of the elements are converted into the corresponding carbides by heating them with an excess of carbon

*Paper presented at the 8th International Congress of Applied Chemistry, New York, September, 1912.

to a high temperature in an electric furnace, the oxygen is given off quantitatively as carbon monoxide. The quantitative formation of carbon monoxide is aided by an excess of carbon at high temperatures, and by a low pressure; also, as has been pointed out by Moissan, the refractory oxides are more readily reduced in the presence of metallic iron.

The details of the method as at present worked out are as follows:

A vacuum furnace of the Arsem type as supplied by the General Electric Co. is employed, and is shown in Fig. 1. The gun metal chamber *A* of the furnace of 20 cu. in. capacity rests inside the water jacket *R*. The cover *B* is fastened to the chamber by means of 18 cap screws, *D*, and the joint is made tight by a rigid lead gasket. The tube *J*, through

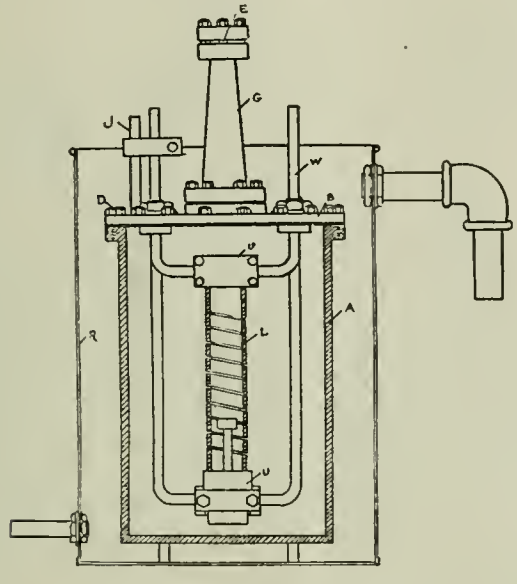


Fig. 1.

which the air is exhausted, is soldered into the cover. The window tube *G* is fastened to the cover by six cap screws, the joint made tight by another lead washer. The mica window *E* is placed in the top of the window tube. Current is led in through the electrodes *W*, which are brass tubes containing running water. The graphite heater *L* is fastened to the electrodes by means of the clamps *U*. The crucible is supported by the stand as shown in the figure and is thus placed in the hottest part of the furnace.

Twenty to twenty-five grams of the sample of metal in which the oxygen is to be determined are placed in a small graphite crucible and about four or five grams of finely powdered graphite added. The crucible is then placed in the furnace, the cover bolted down, and by means of a small rotary oil pump operated in series with a Geryk pump a vacuum of 0.01 of a mm. is obtained in the furnace in less than fifteen minutes. After thoroughly exhausting the furnace, the cooling water is turned on and the crucible and contents heated to about 500°-600° with the pump still running. This is necessary in order to pull away as completely as possible the oxygen absorbed by the heater and crucible. As carbon does not begin to reduce the oxides below 900° there is no danger in heating the crucible up to 500°. After fifteen minutes the furnace is allowed to cool, which it does very rapidly. Nitrogen that has been dried over sulphuric acid and phosphorus pentoxide is now allowed to enter the furnace until the latter is about half full. This is then pumped out and the crucible again gently heated. Only by such a treatment is it possible to reduce the oxygen left in the furnace to a reasonably small value. It seems impossible to pump the absorbed oxygen entirely out of the furnace, but by washing with dry nitrogen it can be almost eliminated.

The stopcock leading to the pump is now turned off and seventy volts applied to the electrodes which causes a current of about 200 amperes to flow through the heater. A high temperature is reached very rapidly, the metal melting in three or four minutes. Just as the metal melts, violent ebullition very often occurs. This is prevented by opening the circuit for a short time and allowing the charge to cool. The metal soon becomes quiet and the heating is continued for twenty minutes. The furnace is then allowed to cool thoroughly, after which fresh air, or better nitrogen, that has been dried over sulphuric acid and phosphorus pentoxide is allowed to completely fill the furnace.

The gas now in the furnace is analyzed for carbon monoxide in the following manner:

The vessel *C* in Fig 2 is exhausted by means of a Toepler pump, and connections made with the furnace as shown in the diagram. The stopcock from the furnace is opened and if the gas in the furnace is under a pressure other than atmospheric, the difference is shown by the differential gage *E*. Correcting the barometric pressure by this amount gives the pressure of the gas inside the furnace. Stopcock *F* is now opened and the vessel and the pump filled with gas. A decrease in pressure corresponding to the volume of gas taken from the furnace is shown by the gage *E*, and we are thus able to calculate the fraction of gas taken from the furnace. By this method we are practically free from any errors due to temperature variation.

The gas is now slowly forced over iodine pentoxide which is heated to 130° C. and here the carbon monoxide is oxidized to carbon dioxide, liberating an equivalent amount of iodine. The latter is absorbed in a 10 per cent solution of potassium iodine and subsequently titrated with *N* 100 sodium thiosulphate.*

A much more simple method of withdrawing an aliquot part of the gas for analysis, if a large quantity of mercury is available, is to use a mercury aspirator instead of the Toepler pump. By replacing the reservoir *C* by a liter bottle which may be filled

*Nicloux and Gautier, Compt. rend., 126, 746; Kinnicut and Sanford, J. Am. Chem. Soc., 22, 14

with mercury, a known fraction of the contents of the furnace may be withdrawn, and forced directly through the iodine pentoxide tube.

The first point to be definitely determined was, how free from oxygen can the furnace and its heating element be made; in order words, using a sample of iron known to be free from oxygen, what amount of oxygen will be shown in a blank experiment? It was found that the oxygen indicated by the iodine liberated from the iodine pentoxide was due to three factors: first, a certain practically constant amount of iodine set free from the iodine pentoxide when air or nitrogen free from carbon monoxide was led over it; second, the actual oxygen absorbed on the walls and on the heater of the furnace; third, the moisture in the furnace.

That iodine pentoxide when heated to 150° in a current of dry air or nitrogen would give up small amounts of iodine has been recognized by previous investigators (L. A. Levy, *Soc. Chem. Indust.*, 30, 1437). We have found that by reducing the temperature to 130° the oxidation of the carbon monoxide is complete, while the decomposition of the pentoxide is reduced to a minimum. By withdrawing from the furnace at each analysis a constant volume of gas and drying the same over phosphorus pentoxide, a uniform blank amounting to 0.006 gram oxygen for the furnace contents was obtained. The weight of oxygen absorbed on the walls of the furnace and in the heater when a vacuum of 0.01 mm. was maintained was found in blank analysis using iron free from oxygen to be 0.02 gram. If the air used to dilute the furnace contents previous to withdrawing the sample of gas for the carbon monoxide determination be not dried over phosphorus pentoxide, the amount of oxygen indicated may rise to 0.035 gram. By first exhausting the air from the furnace, and then filling with nitrogen and re-exhausting the amount of oxygen shown by a blank, analysis was found to be between 0.0120 and 0.0129 gram.

The accuracy of the method, so far as the ability to carry out the operations without introducing errors not corrected for as above, was shown by the fact that a sample of iron or steel containing oxygen may be heated, and the oxygen determined; upon reheating the same charge with additional carbon no further formation of carbon monoxide is obtained.

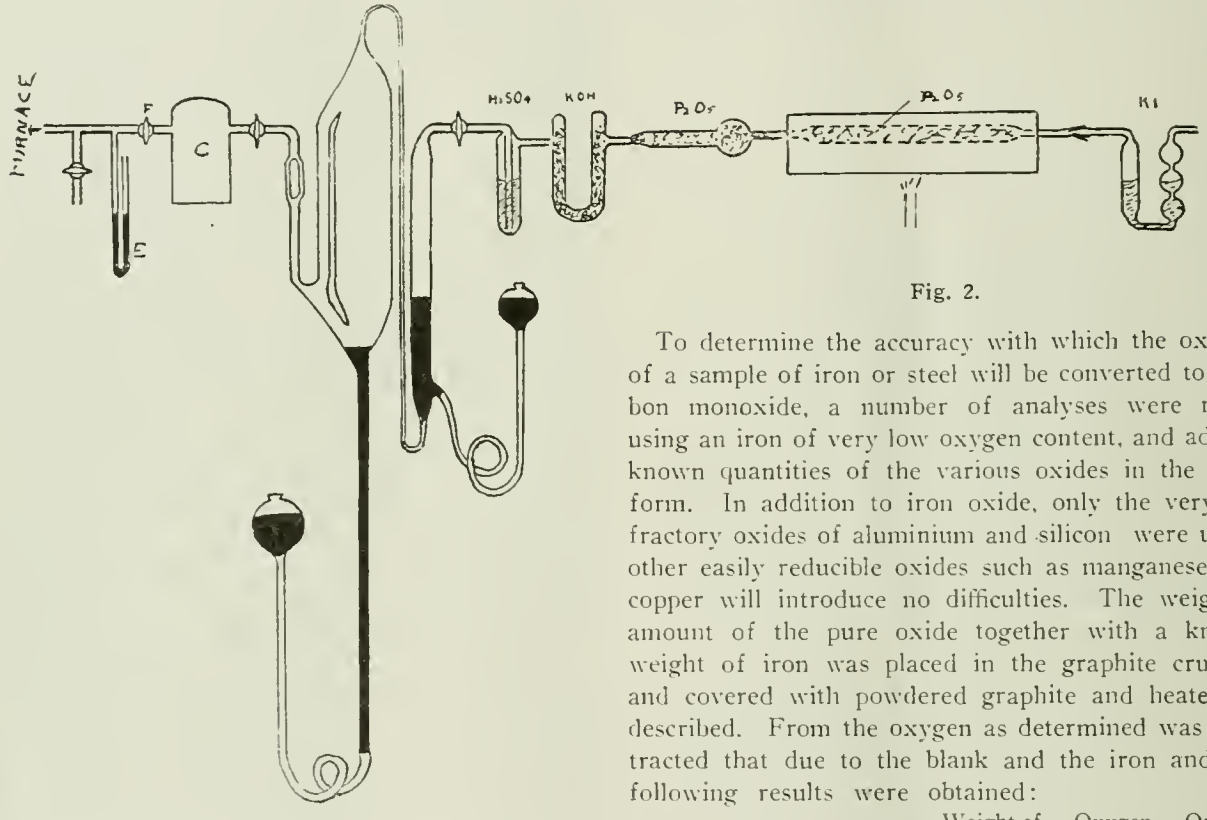


Fig. 2.

To determine the accuracy with which the oxygen of a sample of iron or steel will be converted to carbon monoxide, a number of analyses were made using an iron of very low oxygen content, and adding known quantities of the various oxides in the pure form. In addition to iron oxide, only the very refractory oxides of aluminium and silicon were used; other easily reducible oxides such as manganese and copper will introduce no difficulties. The weighted amount of the pure oxide together with a known weight of iron was placed in the graphite crucible and covered with powdered graphite and heated as described. From the oxygen as determined was subtracted that due to the blank and the iron and the following results were obtained:

	Weight of oxide.	Oxygen calculated.	Oxygen found.
Ferric oxide	0.5650	0.1695	0.1700
Ferric oxide	0.6525	0.1960	0.1940
Ferric oxide	0.8400	0.2520	0.2440
Ferric oxide	0.1516	0.0455	0.0480
Aluminium oxide	0.4925	0.2310	0.2040
Aluminium oxide	0.1860	0.0875	0.0810
Aluminium oxide	0.3065	0.1440	0.1260
Silica	0.0673	0.0360	0.0342
Silica	0.0320	0.0181	0.0171

While the results as obtained are not so accurate as is desired, the reduction being somewhat incomplete, and therefore the results uniformly low, the method has served to explain the discrepancies noted between the oxygen content as determined by the Ledebur method in certain samples and their physical and chemical properties. As examples of such analyses may be mentioned the following:

Sample No. 1 is a special heat of an open hearth steel to which iron ore and an excess of manganese was added in the ladle. The finished steel gave every evidence of having a high oxygen content, although, by the Ledebur method, but 0.006 per cent oxygen was obtained. When determined by the vac-

uum furnace reduction method the real oxygen content of the steel proved to be 0.20 per cent.

Sample No. 2 is a high grade of open hearth steel in which the Ledebur method detected no oxygen. The vacuum method showed that there was 0.09 per cent present.

No. 3, open hearth steel.

No. 4, same as No. 3 but from ingot to which ore was added.

Samples Nos. 5 and 6 represent two ingots from the same heat of open hearth steel of high quality. To No. 5 was added some iron oxide as the ingot was poured. The oxygen content of the ingot giving satisfactory results was 0.065 per cent while that to which the ore was added and which was highly unsatisfactory proved to be 0.31 per cent.

No. 7, open hearth steel

No. 8, open hearth steel.

No. 9, open hearth iron.

No. 10, open hearth iron.

Nos. 11*a* and 11*b* are duplicate analyses of an ingot iron of early manufacture. The vacuum furnace method indicates about three times as much oxygen as the Ledebur method.

Nos. 12*a* and 12*b* are ingot iron of later make and show an oxygen content of but 0.10 per cent. The full analyses are given in the following table:

No	C.	Mn.	S.	P.	Si.	Cu.	O. Ledebur.	O. Vacuum furnace.
1	0.19	0.92	0.052	0.123	....	....	0.006	0.29
2	....	....	....	....	....	....	0.000	0.09
3	0.17	0.65	0.097	0.064	0.017	....	....	0.11
4	0.12	0.17	0.065	0.088	0.015	....	....	0.33
5	0.09	0.18	0.061	0.087	0.019	....	....	0.31
6	0.14	0.24	0.070	0.092	0.009	....	....	0.065
7	0.09	0.33	0.065	0.068	0.006	0.17	0.009	0.021
8	0.08	0.33	0.036	0.070	0.005	0.22	0.010	0.039
9	0.01	0.03	0.050	0.007	0.003	0.20	0.037	0.056
10	0.01	0.04	0.015	0.008	0.004	0.19	0.052	0.064
11*a*	0.01	trace	0.015	0.002	....	....	0.069	0.23
11*b*	0.01	trace	0.015	0.002	....	....	0.076	0.21
12*a*	0.02	0.03	0.029	0.004	0.0014	0.043	....	0.10
12*b*	0.02	0.03	0.029	0.004	0.0014	0.043	....	0.11

It is intended that this paper be considered a preliminary communication, and it is hoped that the method will be both simplified and improved by further work. It is published at this time in the hope that others interested in the effect of oxygen on steel will find in the idea something of value.

Japan's sales abroad of raw silk and silk products in 1912 aggregated nearly $100,000,000. This is the most formidable item in Japan's foreign commerce, and it is a common saying that the country pays its national debts in raw silk and silk products. Every effort is being made by the Japanese to extend the silk industry throughout the world. The total exports of raw silk and silk fabrics of all kinds reached $88,155,559 in 1911, to which upward of $10,000,000 was added in 1912, making the total for the latter year $98,490,202. This increase was more than made up by the sales of raw silk and silk products to the United States, which rose from $47,254,91 in 1911 to $59,563,393 in 1912, all but about $2,000,000 worth being raw silk. Thus, the chief items of commerce between the two countries are raw silk and raw cotton. During 1912 Japan purchased a total of $32,171,375 worth of American raw cotton and the United States purchased a total of $57,243,941 of Japanese raw silk. The great importance to Japan of the American market is illustrated by the fact that of the total exports of raw silk in 1912 ($74,859,957) the United States alone took over 76 per cent. The increase in purchases of this Japanese staple by the United States during 1912 was approximately $12,500,000.

NEW METHOD FOR MECHANICAL TESTS ON CAST IRON.*

By C. FREMONT, Paris.

For a century, cast iron has been tested by bending test bars in the Monge apparatus. At present the most important specifications prescribe two tests: tensile strength and resistance to impact.

One government department recently made enquiries among the iron-founders on its list of contractors, to ascertain what test they considered the most suitable; but the answers received were so divergent that no practical conclusion could be formed. It is therefore interesting to compare the different methods of applying mechanical tests to cast iron. I have already published a first notice on this subject, and today I will complete this investigation by presenting the results of supplementary tests.

This time I proposed to compare the results obtained, from one and the same cast iron, with statical bending, tensile, impact and shearing tests, and then to repeat these tests on a large number of pieces of cast iron of divergent origin.

In order to compare the results of the tensile and bending tests I operated on test 140 bars collected by an important department and derived from different foundries. In the heads of these test pieces I cut out small prisms measuring 8 by 10 by 30 mm., which were subjected to statical bending tests in a machine which recorded the amount of force applied. This machine was described in the former report.

The results have been plotted on the graph (Fig. 1), the abscissæ representing the force required to fracture the test bars in the bending tests, and the ordinates the corresponding tensile strength per square millimetre of sectional area.

In general it is found that two specimens of cast iron with an equal breaking strength under statical bending tests may vary considerably in tensile strength, the ratio being in some cases as high as 2:1.

Since, in the bending test, a prismatic test piece breaks by the tension exerted on the bent portion, one ought to obtain concordant results in both kinds of test (bending and tensile) when applied to the same cast iron, except for the differences due to heterogeneity of the metal. As this is not the case, some other intervening cause must operate.

Now, I have shown in my earlier report that the coefficient of elasticity of cast iron varies between wide limits, being up to three times as much in some cases as in others. Thus, for instance if we take two similar test pieces, one of inferior and the other of very good cast iron, the bend produced under the same load in the bending test will vary according to the quality of the metal, and may be three or four times as great

*Paper presented at the 6th Congress of the International Association for Testing Materials

[1] Bulletin de la Société d'Encouragement Paris, May, 1909. Mechanical tests for cast iron

in cast iron of low quality as in the better quality metal under the same conditions. Owing to this high capacity of elastic deformation, the test pieces of poor cast iron will give in the tensile test, whereas, other conditions being equal, the test pieces of good cast iron break prematurely by flexion. The fact is well known to practical men, for it is often noticed in making ten-

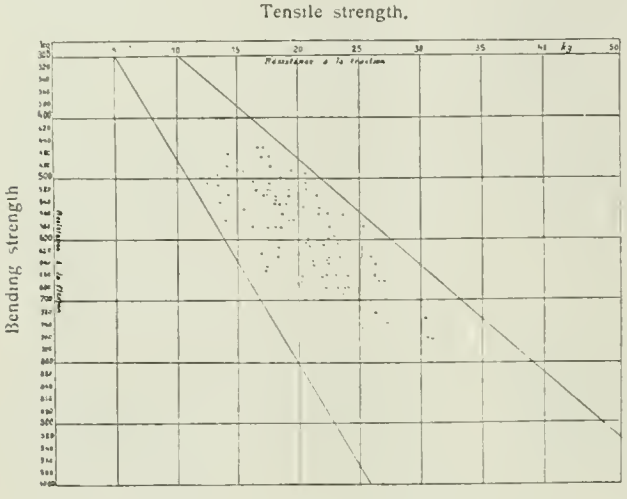


Fig. 1.—Comparison of Tensile and Bending Strength of Cast Iron.

sile tests that the test pieces break in the holders, where the sectional area of the piece is much larger than in the body of same.

It will be evident therefore that if the differences observed in tensile tests (Fig. 1) are due, in the case of bad cast iron, to the heterogeneity of the metal, the cause of the differences cannot be the same in the case of good cast iron, but is due to the low elastic property which is inversely proportional to the strength of the metal.

I have vainly endeavored to correct these deviations from the truth in the tensile strength of the test piece, by placing a pad of copper under each head. To compare the results of bending and shearing tests I have worked with 267 fragments of cast iron, derived in part from test pieces from impact and tensile tests, and in part from old castings.

The results have been plotted on the graph (Fig. 2), the abscissæ representing the force required to fracture prismatic test pieces in the bending tests, as in the previous tests, whilst the ordinates give the corresponding shearing strength per square millimetre of sectional area.

This time we find that a sufficiently complete correlation exists between the two kinds of test: statical bending and shearing. I have made over two thousand tests and have been able to confirm that the differences are entirely due to the heterogeneity of the metal, and that they diminish in proportion as the quality is higher.

In order to compare the results of the impact and shearing tests, I operated on the fragments of 37 test pieces from impact tests carried out by a railway company. These pieces, of square section (40 by 40 mm.), which had been fractured by the impact of a 12 kilo. drop hammer, were sawn so as to furnish two prismatic test pieces measuring 8 by 10 by 30 mm., one being taken from the edge and the other from the middle of the large test pieces, for the purpose of applying bending and shearing tests as in the preceding cases. The necessity for taking two test pieces was caused by the difference in the quality of the metal, the middle portion being weaker in consequence of segregation in the specially cast ingot. The results of these tests have been plotted on the graph (Fig. 3.) In the abscissæ, M represents the results obtained with the test pieces from the middle, and B those taken from the edge of the fragments broken by the impacts produced by the hammer falling from progressively increasing heights, viz.: 40, 45, 50, 55, 60 and 65 cm. respectively. The ordinates give the results of the shearing tests per square millimetre of sectional area.

One sees that there is no relation between the results of the impact bending tests and the shearing or statical bending tests (since we know that these two tests are in harmony). The cast iron specimens which fractured under a low height of fall—45 cm.—gave shearing strengths varying between 10 and more than 21 kilos. per sq. mm.; whilst the specimens which required the comparatively high fall of 60 cm. to produce fracture, gave shearing strengths of 12 to 20 kilos.

This great divergence between the results of the im-

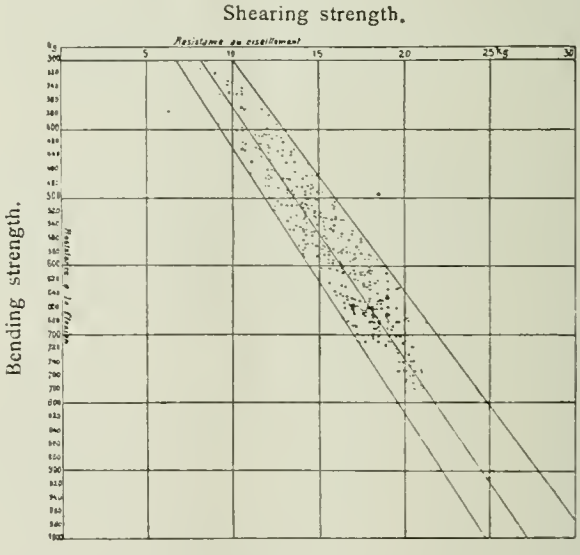


Fig. 2.—Comparison of Shearing and Bending Strength of Cast Iron.

pact tests and of the statical bending or shearing tests is explained by the variation of the coefficient of elasticity in inverse ratio to the tensile strength of the cast iron. In fact, if we take the case of two similar test pieces, one of which, however, is of poor and the other of very good cast iron, the force necessary to fracture them by impact will differ but little, because though the force required to fracture the poor iron is smaller than that needed in the case of the good iron,

the poor iron will bend more under flexion than the good iron, and there will be only a small difference in the product of the two factors, force and deflection, in the two cases. The presence of dust or oxide, forming a pad under the test pieces at the supports, or the use of a lighter anvil base, will constitute a sufficient cause to influence the results of the tests considerably.

It should also be noted that, although the impact test be necessary in the case of iron or steel because these metals, subjected to different conditions, may exhibit different methods of fracture, this test is not essential in the case of cast iron, this kind of metal exhibiting only one method of fracture between the

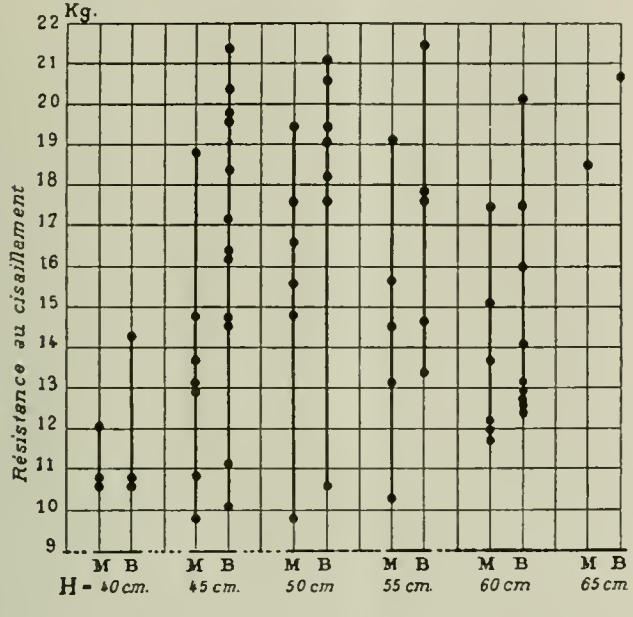


Fig. 3.—Results of Impact and Shearing Tests.

grains, namely granular fracture, no matter whether the test be static or dynamic.

In short, it may be asserted that the impact bending test does not indicate the strength of cast iron; and that the tensile test can never be performed with sufficient accuracy, whatever the care bestowed and the precision of the apparatus, since the test piece can never be pulled in an absolutely axial direction. Statical bending and shearing are the only mechanical tests capable of revealing the quality of cast iron. The manner of taking the sample for testing is also of great importance, and tests applied to a test piece that is cast specially for that purpose will give only approximate information on the quality of the metal.

To obtain accurate information it is essential to take the test piece from the actual casting that is to be ultimately used in practice.

In order to attain this result one must be able to take small test pieces; and this I have done in the majority of instances by boring, in a special manner, holes which are intended ultimately for the purpose of assembling the castings, or else can be plugged up again if found necessary. These holes are 14 mm. in diameter, and are bored by a tool in the shape of a trepan, which leaves in the center a cylindrical core 7.5 mm. in diameter. This core can be broken off with ease at the base, by a small special tool, and can then be shaped into a square prism of 5 mm. side. Shearing tests are applied to the prism at intervals of 3 mm. lengthwise, in order to ascertain the strength at the periphery and various depths

These shearing tests will give accurate information on the quality on the cast iron, with rapidity and economy.

RESEARCH ON THE HARDNESS OF STEEL.*

By CAPTAIN C. GRARD, PARIS.

In 1900, Brinell proposed to the Congress of the International Association for Testing Materials, held at Paris, a special method for determining the hardness of metals.

The method consists in exerting upon the metal a pressure by the intermediation of a steel ball of a given diameter. The impression produced in the metal submitted to these tests has the form of a spherical calotte, and the surface a of this calotte can easily be calculated.

If we call P, the pressure which is enacted on the ball, and a the surface of the spherical calotte, then the expression

$$\frac{P}{a} = \triangle$$ gives the hardness figure.

These hardness tests can be considered from two different points of view.

1. The ball method appears as a substitution of a hardness test for the traction test; this substitution admits of making the acceptance tests both more simple and less expensive, whilst at the same time more numerous, as may be desired.

The hardness test is more economical than the traction test. It can be applied at a considerable number of points, and it admits therefore of testing the metal in parts which are suspected.

The test can notably be utilized for estimating finished articles or specimens which do not, on account of their shape or their dimensions, permit of preparing test rods for traction experiments.

The coefficient of proportionality allows in the case of ordinary carbon-steels to draw conclusions as to their strengths.

Applied in this way the ball method does not furnish other information than the traction test, but it gives that information in a more rapid and more simple way.

2. The ball method may be an original method of a particular character revealing a special property, viz., homogeneity.

*Paper presented at 6th Congress of International Association for Testing Materials.

A perfectly homogeneous metal should indeed, when submitted to the ball test, yield identical impressions, provided the experimental conditions be rigorously the same, and that the measurements can be conducted with all desirable precision.

But the hardness numbers are never identical. They differ from one another by variable quantities. The discrepancies are caused both by errors committed during the experiments and measurements and by the want of homogeneity of the metal.

When we fix the part due to the experimental errors, we shall have a sufficiently precise knowledge of that part which must be attributed to the defective

Fig. 1.

homogeneity. We shall then possess in the ball method a valuable means of controlling this defect, which has so important an influence in dealing with steel.

The diverse series of tests which are enumerated below have been made on carbon-steels previously submitted to appropriate thermal treatments. The tests permit of responding in a certain measure to the desire which was formulated by the Copenhagen Congress concerning the control of the homogeneity and the determination of the strength by hardness tests.

It has moreover appeared interesting to put the hardness and the brittleness of the steels in question on parallel lines.

DETERMINATION OF THE HARDNESS NUMBER OF ORDINARY ANNEALED CARBON-STEELS.

Control of the Homogeneity.—The experiments made have demonstrated that the ball in entering into the metal under a pressure of 3,000 kg. produces a protrusion of the metal.

Fig. 1 shows a general view of the section through an impression.

When we call D the diameter of the ball, d the diameter of the impression, h the depth of this impression, the expression for the surface of the spherical calotte will be:

$$a = \pi Dh \qquad \text{or:}$$

$$a = \pi D \frac{D - \sqrt{D^2 - d}}{2}$$

We can therefore:

1. Measure h, the depth of the impression, and deduce a from it; or

2. Measure d, the diameter of the impression, and deduce a from it.

In view of the particular shape of the edge of the impression it is interesting to study the difficulties which are encountered in each of these modes of procedure and to put forward the advantages and the inconveniences which each method carries with it.

Selection of the Process of Evaluation.—The two errors likely to be committed, viz., the first, exaggeration of the depth of the impression by taking this depth to be equal to $h + \epsilon$, that is to say, by making allowance for the bulging up, and the second, by starting from a diameter which is vitiated by virtue of the ovalization of the ball — are errors of the same order.

The two methods of procedure, indeed, lead to results which are practically identical.

By the first method we find the hardness numbers for certain steels:

Soft steels	$\Delta = 142$
Semi-hard steels	$\Delta = 166$
Hard steel	$\Delta = 201$

and by the second method:

Soft steels	$\Delta = 142$
Semi-hard steels	$\Delta = 166$
Hard steels	$\Delta = 200$

As we are at liberty regarding the choice of the two methods, we have chosen the latter which has furnished very interesting information.

Influence on the Value of the Hardness Number.—The causes which may exercise their influences on the value of the hardness number may be divided into two distinct groups:

(a) The first group comprises the influences exerted by the more or less high precision of the apparatus used, and the errors which are inherent to these apparatus, viz.:

1. Errors committed in evaluating the pressure;

2. Errors committed in measuring the diameter of the impression.

The author has hence determined the precision upon which we may rely in making use of the apparatus.

(b) The second group comprises the influences which the experimental conditions in themselves exert upon the value of the hardness number. It will be advisable to state these experimental conditions in a very clear manner.

The want of method and of uniformity in the execution of the tests is indeed likely to cause frequent discrepancies and to prevent the results from being intercomparable.

From this point of view the author has studied:

1. The influence of the rapidity of applying the pressure of the machine which is to produce the impression.

2. The influence of the duration of the pressure application.

3. The influence of the sense in which this pressure is enacted in respect to direction of the rolling.

4. The inference of the selection of the diameter of the impression on which the measurement is made.

The adoption of a rational and uniform method for carrying out such tests admits of eliminating the second source of errors.

The first source will alone remain.

After having conducted numerous experiments we shall be able to make an allowance for the maximum error which is likely to affect the hardness number.

In a perfectly homogeneous metal the figures which correspond to the several impressions should not differ

from one another by a quantity superior to the maximum admissible experimental error.

The determination of this maximum error therefore furnishes the means of controlling the homogeneity of the metal by means of the hardness ball test.

First Group of Errors.—The sum of the maximum errors due to:

1. The evaluation of the pressure with a direct reading machine (one Brinell unit maximum).

2. The reading of the impression with the aid of the

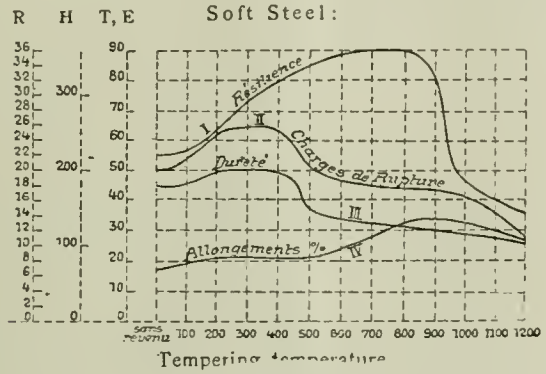


Fig. 2.—Variation of Mechanical Properties of Soft Steels.

microscope (3 Brinell units maximum) has been found inferior to 5 Brinell units.

Second Group of Errors.—Influence of the rapidity of the application of the pressure. With a rate of applying this pressure of two minutes and more the diameters of the impression vary very little.

A rate of applying the pressure within two minutes may therefore be adopted for all the tests.

Influence Exerted by the Duration of the Pressure. —For precise experiments a period of five minutes for keeping the pressure on seems to constitute a minimum below which one should not go.

In any case if we should choose a smaller period in order to proceed more quickly, it will be necessary to adopt a uniform period for all the tests in order that the tests may be comparable.

3. Influence of the annealing and of the sense in which the pressure is applied with regard to the direction of the rolling.—The conclusions to be drawn from these experiments are the following:

1. A complete methodical annealing has the effect of suppressing the results of the cold work done in rolling, it softens the steel, and it leads in general to a larger diameter of the impression than that which would have been found before annealing, that is to say, to a smaller hardness number.

It is therefore necessary to submit two different steels to an annealing process previous to comparing their hardness numbers with one another.

2. Impressions made at right angles to the direction of rolling are larger than those effected parallel to the rolling.

The hardness numbers which result from the former tests are smaller than those which are found in the latter tests.

It is therefore necessary well to specify the sense in which the impressions have been produced, in order to render the results comparable.

We shall revert to this point when speaking of the coefficients of proportionality.

3. Whether the impressions be made at right angles to or parallel to the direction of the rolling, it is indispensable to specify the diameter, the measurement of which is to serve as basis in the estimation of the spherical calotte of impression.

When a certain number of diameters are measured in one and the same impression, it will be found that these diameters are not all equal, and there exist sometimes between them differences of several hundredths which cannot altogether be ascribed to errors of measurement.

Rolled Steels.—Tests made at right angles to the direction of the rolling.

In these impressions the diameters which are parallel to the sense of the rolling have in general been smaller than the diameters which are at right angles to this direction.

In the case of certain steels this difference has attained the value of 5 hundredths in a regular fashion.

It appears necessary to ascribe this difference to the

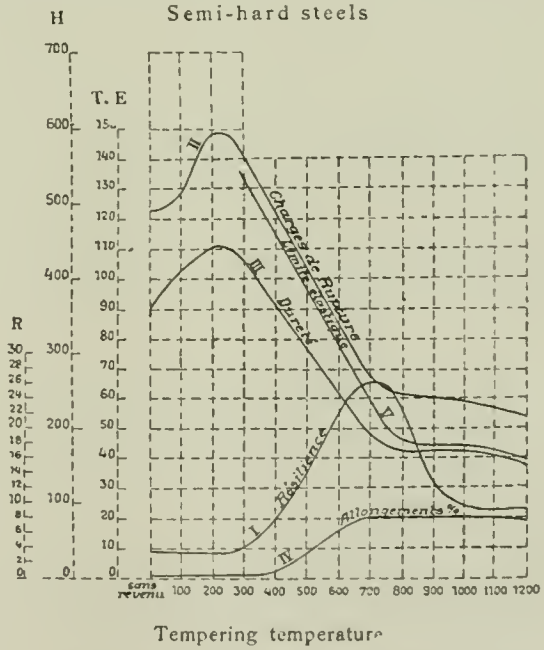


Fig. 3.—Variation of Mechanical Properties of Semi-Hard Steels.

difference in the strengths of the metal in the transversal and the longitudinal directions, a difference which is also brought out by traction tests.

The two diameters which are measured along the bisectrices of the two just-mentioned diameters have always been practically of equal lengths. We see that, in order not to introduce any errors into the assessment of the hardness figure, we should be very care-

ful in precisely fixing the orientation of the diameter on which the measurement is to be made. Experiments carried out in a direction parallel to the sense of the rolling have led to analogous observations.

Cylindrical Steel Bars.—When we make the hardness tests on sections of bars or on cylindrical blooms, it is advisable to choose the diameters serving for conducting measurements as follows:

Either take diameters situated on the radius of the section passing through the center of the impression;

Or the diameters at right angles to those just mentioned.

In any case it will be advantageous to take, as value of the diameter serving as basis in the calculations of the impression, the means of the diameters previously spoken of.

Moulded Steels.—The impressions made in moulded steels have, one may say, been rigorously circular.

We do not find any of the differences noticed in the diameters of rolled steels.

In moulded steels there is indeed not any orientation of the molecules such as we find in rolled steels.

When we exert the pressure at a certain point of the moulded steel, there is equality of resistance in all the directions starting from this point.

Conclusions.—In adopting the experimental conditions which we have defined, we shall eliminate the discrepancies and the errors which might result from a want of method and of uniformity in conducting the tests.

We therefore are merely faced by the errors of the first group, errors which finally come down to a modification of the diameter of the impression.

En résumé, with apparatus analogous to those we have described and under the conditions as defined, the maximum error in absolute value, which may arise in estimating the hardness number, will be below 5 Brinell units.

If then N be the exact hardness number corresponding to a certain steel, N+5 will represent the variations which may be imputed to the experimental errors.

Two hardness numbers relating to two impressions made in the same perfectly homogeneous steel should not differ by more than 10 units.

Differences greater than 10 units must be ascribed to a variation in the distribution of the constituents of the metal.

We therefore have in our hands a valuable process for controlling the homogeneity of a certain metal.

That is the important conclusion which may be drawn from the first part of the research which we have undertaken.

RELATION BETWEEN THE HARDNESS AND THE TENSILE STRENGTH.

Coefficient of Proportionality Applicable to Annealed Steels and to Hardened Steels.—When we call R the resistance, the tensile strength of the metal and Δ the hardness number (Brinell number), we have the relation established by Brinell:

$$\frac{R}{\Delta} = K$$

in which K is a coefficient which will undergo little variation for different kinds of carbon-steel.

This fact can experimentally be verified in the ordinary way.

The fact is of interest because it admits of simplifying traction tests.

It will suffice indeed to measure the diameter of the ball impression, to deduce the hardness figure from this impression, and finally to multiply this hardness number by the coefficient of proportionality in order to arrive at the tensile strength.

These operations are simple and they dispense with the necessity for the always laborious preparation of test specimens.

But the coefficient of proportionality is not absolutely constant. It undergoes slight variations with different grades of steel, variations which it will be interesting to enquire into. We shall study in succession annealed steels and hardened steels having passed through different processes of tempering.

(a) Annealed Steels—The ordinary carbon-steels may be divided as follows:

Extra soft steels, R ranging from	34 to 40 kg
Soft and semi-hard steels, R ranging from	40 to 55 kg
Semi-hard steels, R ranging from	55 to 65 kg
Hard steels, R ranging from	65 to 75 kg
Extra-hard steels, in which R >	75 kg

VARIATION OF THE MECHANICAL PROPERTIES OF CARBON-STEELS WITH THE TEMPERING TEMPERATURE

A large number of traction tests have been made in parallel with hardness tests, for each of these grades of steel.

The tests have enabled us to determine the coefficients of proportionality.

1. Hardness Tests Made at Right Angles to the Direction of Rolling.—According to these tests the carbon steels may be divided as follows, with regard to their hardness:

Steels, extra soft	$\Delta < 120$
Steels, soft and semi-hard	$120 < \Delta < 160$
Steels, semi-hard	$160 < \Delta < 180$
Steels, hard	$\Delta < 120$

The coefficients of proportionality corresponding to the different grades are the following:

Steels, extra-soft	K = 0.360
Steels, soft and semi-hard	K = 0.355
Steels, semi-hard	K = 0.353
Steels, hard	K = 0.349

(b) Hardened and Tempered Steels.—The steels in question, except extremely extra-soft and extra-hard steels, have been submitted after hardening to tempering and annealing processes at temperatures ranging from 100° up to 1200°. For each thermal treatment hardness tests and tensile traction tests have been carried out in parallel.

It has been possible to arrange the results synthetically in tables according to the means of a great number of tests.

The curves of hardness and of tensile strengths represent the general trend of the phenomena for steels of each class having respectively the average properties of the class to which they belong, viz.:

Soft or semi-soft steels..... R = 44 kg
Semi-hard steels..... R = 60 kg
Hard steels..... R = 70 kg

In order to obtain the coefficients of proportionality it has been necessary to bring together average strength—curves with average hardness—curves as es-

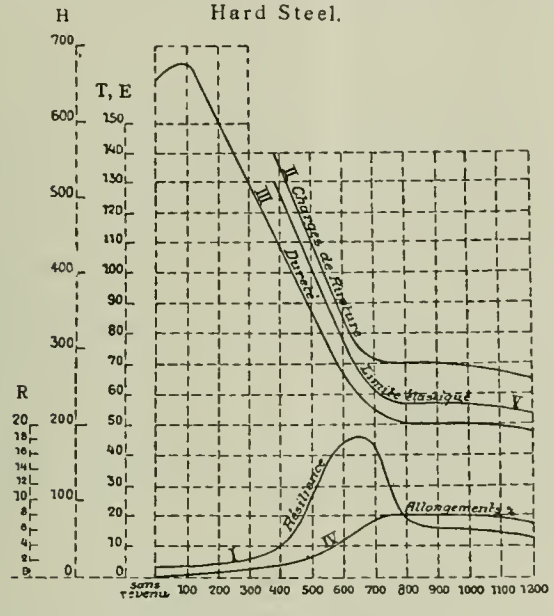


Fig. 4.—Variation of Mechanical Properties of Hard Steel.

tablished by numerous impression measurements, conducted on steels of the indicated grades tempered to different degrees.

For the same specimen of a steel and for the same thermal treatment there have been taken about 20 impressions.

The trends of the two curves are practically the same.

The comparison of the two curves justifies the following remarks:

Hard Steels.—In the case of the hard steels the impressions made at different degrees of tempering have shown a very great regularity.

The discrepancies observed between the impressions have in general amounted to one or two hundredths, with the same degree of tempering.

It has hence been possible to determine the hardness curve of these steels in a continuous fashion.

In the case of the hard steels the traction curve is, on the contrary, very difficult to determine between no tempering and tempering at 400°, because the bars break owing to brittleness.

For this interval the hardness curve can therefore yield information which the traction curve cannot supply.

This curve brings out a maximum of hardness for tempering at about 100°.

Coefficient of Proportionality of Hard Tempered Steel.—The coefficient of proportionality of the hard tempered steel which has undergone tempering between 500° and 600° has been found to be 0.318.

We have previously stated that the coefficient of proportionality of hard annealed steel has been found to be 0.349.

Semi-Hard Steels.—The semi-hard steels have often given rather irregular impressions for the tempering range nil and 500°.

Coefficient of Proportionality of Semi-Hard Tempered Steel.—The coefficient of proportionality of semi-hard steel which has been tempered between 500° and 600° has been found to be 0.344.

We have already seen that the coefficient of proportionality of the semi-hard annealed steel has been found to be 0.353.

Soft Steels.—Soft steels lead to the same observation as the semi-hard steel as regards the regularity of the impressions when tempered at moderate temperatures.

Coefficient of Proportionality of Soft Tempered Steel.—The coefficient of proportionality of the soft tempered steel, having undergone tempering between 500° and 700°, has been found to be 0.346.

We have previously stated that the coefficient of proportionality of soft annealed steel had been found to be 0.355.

Relation Between the Hardness and Brittleness for Ordinary Carbon-Steels and Special Steels.—It is interesting that we are able to impart to a steel by an appropriate thermal treatment:

1. Hardness.
2. Impact strength or absence of brittleness.

The hardness is determined by the method of Brinell.

The absence of brittleness can be revealed by impact tests conducted with the aid of a Charpy tap of 25 kg, permitting to determine the number of kilogramme-metres required to effect the rupture of a notched bar of 10×10×60.

To associate a great hardness with a great resilience to shock, that is to say, a high Brinell number with a considerable resilience, that should be the aim to be pursued, notably in the case of tool steels.

Even in the case of special steels we have always to consent to making a sacrifice with regard either to hardness or to resilience, according to the object in view.

In most cases we shall have to content ourselves with associating an average hardness with an average tenacity, these two properties being revealed by the methods above indicated.

The results which we have obtained have been summarized in tables which indicate what one might in a general way expect from an ordinary carbon-steel.

Hardness supplemented by resilience can only be obtained by having recourse to special steels.

These tables lead us to the following remarks:

Note 1.—It is preferable, wherever possible, that is to say, when strains are not to be feared, to submit the metal for its regeneration to a tempering which is followed by annealing, rather than to a simple annealing.

By the first mode of procedure the characteristic ρ or resilience (in a general fashion) and $\triangle$ or the hardness figure (frequently) become greater.

Note 2.—The maximum hardness numbers ordinary hard hardened steels ranges from 600° to 650° (hardening without tempering to tempering at 200°).

To this hardness number corresponds a very feeble resilience.

For the extra-hard ordinary steels the maximum hardness number is about 700 (hardening without tempering practically).

The corresponding resilience is practically nil.

When we wish to combine a hardness of this order with a certain resilience, we must add certain constituents to the steels, that is to say, have recourse to special steels.

Note 3.—The steels we have studied have shown in a general way their maximum resilience after hardening and after tempering at a temperature about 50° below the point, A_3 as defined by Tchernoff.

Annealing up to the point A_3 following hardening has given a less strong resilience than that realized by the preceding treatment.

Note 4.—The study in question permits of introducing into specifications the results of hardness tests, joined to brittleness tests, and these characteristics often define the qualities to be required of a metal in the best fashion.

A steel for forged moulds for instance should satisfy the following conditions:

Test before hardening	$\triangle > 250$
	$\rho > 6$
Test after hardening without tempering	$\triangle > 800$
	$\rho > 2$

These are the practical and industrial conclusions to be deduced from this investigation.

The exportation of beef from the River Plate during 1911 surpassed that of 1910 by 40 per cent, while the increase for the past year, as compared with 1911, was only 3 per cent, which does not pertain to Uruguay, as that country sold in 1912 three times the quantity of 1911.

There are three plants in Norway that manufacture ferrosilicon, as follows: The Hafslund Sulfitfabrik, Hafslund, Sarpsborg; the Kellner-Partington Paper Pulp Co. (Ltd.), Sarpsborg, and the Almindelig Elektro-Metallurgisk Co., Christiania. The first-named plant is now controlled by the Kellner-Partington company. The chief business of both these companies is the manufacture of wood pulp, of which they are among the largest producers in the world.

NOTES ON THE BRITTLENESS TEST.*

BY M. DERIHON.

As a matter of probable interest we communicate a number of observations collected in the course of our experience since we began to make use of the brittleness test as a standard method for our steels and forgings.

Since 1904 we have used the drop weight and Frémont test piece for our tests, and we may state at once that our experience of both has been such that we have decided not to abandon them.

We may say that our laboratory, though complete enough so far as mechanical tests are concerned, is not a scientific laboratory, but serves as a guide in close relation with the manufacturing department.

At present, apart from the chemical analyses, tensile tests, ball tests, etc., we have to apply the brittleness test to 80—100 tons of steel per month, bar by bar; and if we add that we leave a test piece for the brittleness test on each article of a certain class of goods that we produce, such as steering swivels and steering levers for motor cars, it will be easily imagined that we have to test about 10—12,000 pieces every month.

It will be evident that in this way we have acquired a certain experience in this kind of test, and have been enabled to form certain conclusions of a practical character.

In the first place, is the brittleness test as stringent and misleading as is generally believed?

No, on the contrary we believe that after a few attempts it is possible to make all steels of good medium quality non-brittle.

The whole question is merely a matter of heat treatment.

Evidently, steels burdened with sulphur and phosphorus, ot rotten with piping, will always remain brittle whatever one may do; but a good ordinary steel, properly treated, is nearly always non-brittle.

At the commencement of our tests, as at present, we used, in addition to certain fine, high-grade steels, a large number of open-hearth steels of various grades, the quality of which always remained approximately the same.

Well, at the outset we had to reject for brittleness 20, 30 and even 40% of the pieces tested, whereas at the present time we find that the total number of rejections in 1911 did not exceed an average of 3 per 1,000.

This results entirely from the progress which these tests have enabled us to make in the application of heat treatment to our steel forgings. Our deduction therefore is that the brittleness test has done us good service by affording us the means of arriving at such homogeneous results.

*Paper presented at 6th Congress of the International Association for Testing Materials, New York, 1912.

Finally, can it be said that a test which gives rise to only 0.3% of rejections is incapable of being employed in practice?

Evidently one must become familiar with the impact test, and not attach undue importance to variations caused in toto by the heterogeneity of the metal.

A certain grade of steel must be classed as brittle when, for instance, the resilience is shown by the test to be less than 20 kilogrammetres, and as not so when the results are more favorable; but one must not seek to grade the quality in accordance with the values obtained.

In our opinion, it is the search after this precision which has led to the large test-piece being selected at the expense of the small one.

The former, of much greater sectional area, evidently gives mean results which are more easily comparable and apparently more rational; but it is attended with the defect of being incapable of showing up the weaknesses of the material, which are pitilessly exposed by the small test-piece assisted by macrography.

Being desirous of settling the point, we selected 6 bars from a parcel of steel which had been rejected in consequence of the tests on Frémont test pieces, and from each bar prepared two 30 by 30 mm. test pieces of the Copenhagen type, with which we obtained the following results in the Charpy apparatus:

Bar Nr.	1	7.5	kilogrammetres	and	7.5	kilogrammetres
" "	2	23	"	"	25	"
" "	3	7.5	"	"	8	"
" "	4	23	"	"	20.5	"
" "	5	41.7	"	"	41.7	"
" "	6	75	"	"	75	"

If these bars were to be rejected on account of giving values below 20 kilogrammetres, then only the bar No. 3 would be thrown out, and perhaps No. 4 as well. However, they were all bad since, independently of the Frémont test, which had condemned them, macrographical examination revealed the presence of serious pipings.

Hence, we do not think it rash to conclude that, without the Frémont test, we should have been led to employ steels of bad quality.

The large test-piece is evidently not always optimistic, and reveals certain causes of brittleness; but in our opinion it does not always expose them and with the same rigor as the small test pieces.

But since the causes of brittleness in steel are often local it would seem preferable to isolate them rather than conceal them in the mass of the metal.

So far as concerns ourselves, one serious reproach we address to the 30 by 30 mm. test piece is that it cannot be used in the case of the forgings we produce, owing to its large size.

We are well aware that the Copenhagen Congress recommends in such cases the use of the 10 by 10 mm. test piece, nicked half way through; but we must confess we should have preferred to keep to the Frémont type of test piece, 10 by 8 mm. with a 1 mm. nick.

In the first place, being flat, this test piece presents the advantage of enabling the direction of the fibres of the metal to be traced. It is also less expensive and less difficult, the small hole terminating the nick of the 10 by 10 mm. test piece being difficult to make readily; and we are acquainted with several laboratories in which the use of this nick has been abandoned on account of the difficulties experienced in the shop.

As for the sharp edges of the nick, we must confess that we have never troubled about them. On no occasion, in the large number of tests performed, have we found any of the unfavorable results to be due to the nick. When a test piece breaks under a low strain, it is because the steel is brittle; and since we have now only 0.3 per cent. of rejections, we think these minor points may be neglected.

Finally, although we have no desire to reopen the discussion as to which apparatus should be used for the impact test, we take the liberty of expressing our opinion, which is based, not on scientific considerations, but on personal experience of forging and stamping machines.

Frémont claims that his drop weight, or similar appliance, is alone capable of revealing brittleness in all cases. In our opinion he is right, and for the following reason.

We believe in the drop weight, because our forgings are made under the steam hammer and drop hammer; and we find that the velocity of the impact and the quantity of the mass receiving the impact are of prime importance.

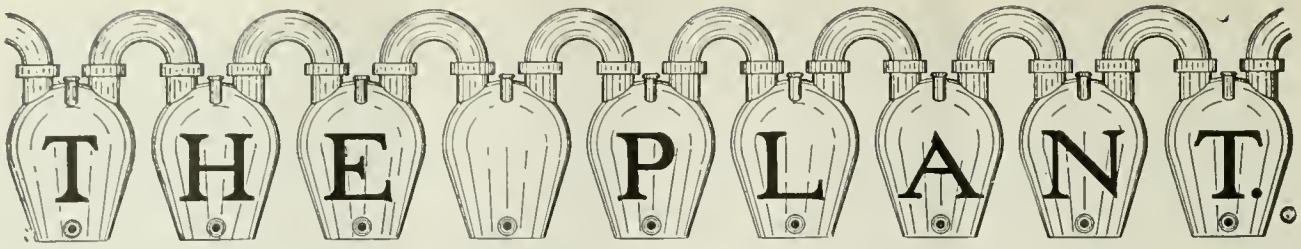
The importance of these two factors is such that it is they which practically limit the work of our drop hammers.

The matrices, being made of very hard, and more or less brittle steel, will not stand, but are constantly breaking, if the height of fall be too great or the impact is too sharp. On this account we have therefore been compelled to reduce the height of fall, increasing the weight of the falling mass, and arranging under the anvil bed a foundation of wooden baulks, so as to take up the impact elastically.

This, however, is accomplished at the expense of the useful effect, since a weight of 500 kilos. falling from a height of 4 metres, is more economical than one of 1,000 kilos. falling a height of 2 metres.

We believe therefore, as Frémont has said, that an apparatus which does not give sufficient velocity of impact or in which the anvil bed is not sufficiently heavy, cannot reveal the brittleness of the test metal in all cases.

The conclusion we draw from this is that, as was wisely decided by the Copenhagen Congress, the Congress should abstain from prescribing any special type of apparatus for performing the impact test: but that it should direct attention to the importance, with regard to the results, of the velocity of the impact and the mass of the anvil bed receiving same.



THE WASTE LIQUOR FROM SULPHITE PULP MILLS.*

By PROF. W. O. WALKER.

This is a subject which one naturally hesitates to present to an audience because the presentation must necessarily consist, for the most part, of an enumeration of a lengthy list of futile attempts at solving the problem. However, some encouragement is secured when one considers the importance of this subject, especially since it is becoming one of the largest sources of waste in Canada. The problem dates back to the beginning of the sulphite pulp industry, and has assumed such acute proportions in some countries that legislation has been enacted with regard to the disposal of this waste and mills have had to be shut down. That condition of affairs has not yet arrived in Canada, mainly on account of its large rivers and sparse population. Since for every ton of pulp produced an equal weight of wood goes into solution, an enormous quantity of organic material is wasted when pulp mills turn out from fifty to several hundred tons of pulp per day. The United States Geological Survey estimates that there are more than a thousand million pounds of this organic matter annually discharged into the streams of the United States.

The waste liquor is usually discharged into rivers, and on account of its great volume and high content of organic material there it becomes a source of pollution, renders the water injurious to health, unfit for boiler purposes, and injurious to fish or other life. It causes in many cases the development of algæ, and in the smaller rivers the stream beds are sometimes completely choken with them. Under certain conditions these sulphite wastes develop large quantities of sulphuretted hydrogen, entailing a rapid loss of dissolved oxygen and the death of all animal and plant life in the stream.

There are three different types of waste from the sulphite paper industry: (1) digester liquor and waste water; (2) screen or filter press water; (3) condenser water. The first two are objectionable, the strong digester liquor being the more so.

As it comes from the digesters it is a dark reddish-brown liquid of variable specific gravity about 1.05. It has a peculiar, not unpleasant odor, due to bodies of a terpene nature. By evaporation of the liquor a syrup is obtained which, on further evaporation, changes to a gluelike mass. The dried residue is about 10 to 12 per cent of the weight of the original liquor. This residue on ignition gives about 12 per cent of ash, chiefly sulphates of calcium and magnesium. The other 88 per cent is organic material.

The following substances have been shown to be present in the liquor:

1. A small quantity of sulphurous acid.
2. A very small quantity of sulphuric acid.
3. As the chief constituent, an organic sulphur compound containing calcium, probably a calcium and magnesium lignin sulphonate.
4. Small quantities of pentoses and pentosans.
5. Mannose, dextrose, and galactose in very small amounts.
6. Free furfural.
7. Traces of vanillin, or a vanillin-like body.
8. Small quantity of a terpene-like substance.:
9. Small quantity of free sulphur.

The chief constituent of this liquor may be precipitated by alcohol. It comes down as a dark, gummy mass which becomes brittle by drying. It may also be obtained by concentrating the liquor to a suitable degree, and then salting it out by means of sodium chloride or magnesium sulphate. Concentrated mineral acids precipitate it, as does also lead acetate. The purification of the precipitate is very difficult since it dissolves, apparently, only in water and dilute alcohol, from which it does not crystallize. It yields brominated and chlorinated derivatives, it contains an active carbonyl group and methyl groups, and is a strong reducing agent. The sulphur has been shown by McRae of this university to be in the form of a sulphonic group. This substance, no doubt, is the soluble reaction product from the calcium and magnesium bisulphites on the complex of groups in combination with the cellulose in the lignocelluloses. These groups are commonly designated as lignin or lignone. Their leading characteristics are those of diketones, or more particularly, quinones. The lignone complex is a body of much higher carbon content than cellulose (44 per cent). The soluble by-products which are, in effect, the lignones in combination with the bisulphite residues, have been separated in various derivative forms and analyzed. The empirical formula of $C_{24}H_{24}(CH_3)_2SO_{12}$ has been established for the product precipitated from the waste liquor by hydrochloric acid. The formula of $C_{24}H_{24}(CH_3)_2O_{10}$ has been given to the parent lignone complex.

*Paper read Feb. 28, 1913, before the Canadian Section of the Society of Chemical Industry.

Our knowledge of the structural relations existing in the lignone group is very limited. What knowledge we have has been gathered from decomposition reactions which are extraordinarily complex and difficult of interpretation. Without entering into particulars in regard to the characteristics of these decompositions with various reagents, it may be stated that they indicate the presence in the lignone complex of hydrocarbon nuclei of very small dimensions together with a high proportion of CO groups alternating in periods of short dimensions with the hydrocarbon groups. Furfural derivatives appear to be present. The presence of CH_3 groups is indicated, as well as a low proportion of OH groups. Apart from these facts the structure is as yet unknown.

In most plants some treatment is given to the waste before it is discharged into the stream. This consists usually in the removal of the fiber and a partial recovery of the sulphur, or merely neutralization. A large mill in Germany is attempting the disposal of its wastes by cooling and neutralizing them, and then discharging them into the city sewers, where the wastes mixed with the domestic sewage are treated on underdrained areas of sandy soils. Another method tried is to cause the liquors to enter sink holes, and mingle with the ground water. This is possible, of course, only where geological conditions are favorable. The substance resulting from the evaporation can be burned in suitable furnaces, and it is claimed that the calorific value is slightly greater than the heat required to evaporate the liquor, the cost of evaporation averaging about 82 cents per 1,000 gallons. A number of patents have been taken out for the recovery of sulphur, but the recovery is incomplete since most of the sulphur is combined organically. A process for the destructive distillation of the residue has been patented, but the yield of useful products is too low for economical development. The yield of oxalic acid by fusing the residue with caustic potash has also been found too low. By adding a solution of gelatin to the liquor, a compound has been precipitated, which, when dissolved in weak alkali, has been employed for engine-sizing paper. The sodium salt of ligninsulphonic acid has been produced and employed as a reducing agent in chrome mordanting wool to replace tartaric and lactic acids. The concentrated liquor has been used as an adhesive in foundries for core making. A slag meal rich in phosphorus has been added to the concentrated liquor and used in fertilizing land. It is asserted that this renders the phosphorus available as plant food. Patents have been granted for processes involving the use of the liquor for tanning purposes. It has been found that 28 per cent. of the solids is removed by hide powder, but this does not necessarily prove the presence of tannin. It has been found that the liquor in itself is not suitable for tanning, but it is being used at present in conjunction with tanning extracts, and serves the purpose of a filler for the leather.

R. T. Mohan investigated the subject of tanning at this university, and found that the addition of lactic acid to the liquor improved the tanning properties. He tried the effect of the addition of sulphites and acids on ordinary hemlock bark liquor, finding that they caused swelling, bleaching, and hardening of the leather. He also tried the effect of an addition of sulphites to waste sulphite liquor and found swelling, hardening, and bleaching to occur. He removed the lime and found very little difference in quality of the leather. Removal of the gummy matters destroyed all tanning property, further the gums when redissolved would not tan. However, the addition of lactic acid improved the tanning markedly. During this work it was noticed that according to the different percentages of acid in the liquor, the leathers varied from hard and bleached to black and flabby. Experiments were carried out to determine what relation of tannin to acid was best to produce leather of a good color and texture. It was found that each acid has a factor for each tanning extract. With bark liquors the best ratio was found to be 0.8 (tans 8°, acid 10) for lactic acid. For sulphite liquors the ratio was 1. For equal parts of sulphite liquor (spruce) and quobracho, the ratio was 0.4. From this it would seem, therefore, that for heavy leather, when acidity of liquor is needed, more uniform and reliable results could be obtained by the proper control of the ratio of acid to tannin in the first half-dozen vat liquors at least. The concentrated liquor has been used to some extent as a binder in coal dust briquetting. It has not proved to be a success, however, partly because of the high percentage of ash, and the fact that the material is not waterproof. It has even been used in combination with molasses and straw as a cattle food.

Most of the uses that have been proposed have been abandoned, either on account of the cost, or of unsuitability for the purposes intended. During the winter of 1910 and '11 an investigation into the possible use of the liquor for laying the dust of roads was carried on at this university by R. T. Mohan. Small sample roads were constructed in imitation of the common macadam road. A layer of road dust was placed on top. Three such roads were treated, one with ordinary road oil, another with the same quantity of concentrated (4:1) waste liquor, and the third with road oil, followed by waste liquor. These roads were treated with water at intervals of a few days for a period of four months, using a total of ten inches of water, the most at any one time being 2½ inches. These figures correspond closely to the total and maximum rainfall in Ontario during May, June, July, August and September. The result was that the oil on the first road was practically all washed away, while the second road that was treated with the liquor, and the third road treated with liquor and oil, still presented a hard surface, which after being broken and dried showed very little dust, and did not have the disagreeable odor given off from the oil-treated road. This experiment gives promise of the material finding use in the treat-

ment of roads. The cost, especially in the neighborhood of pulp mills, should not be prohibitive. Phelps, of the U. S. Geological Survey, carried on a series of experiments to determine if condensation products could be obtained by treating the liquor with aromatic amines. These experiments were based on the assumption that aldehyde groups are present in the organic part of the liquor. He found that, of the amines tried, those retaining the NH_2 group gave bright red products, and those in which substitution had taken place in the NH_2 group gave brown or black compounds. Attempts to diazotise these products failed. When nitrated they gave different colored products, depending upon the amine used. Some of these substances were brilliant dyes. These reactions were carried out without purifying the original amine condensation products. Phelps failed to purify these as he was unable to prevent their decomposition. McRae, of this university, succeeded in preventing this decomposition in the case of aniline by treatment with bromine.

He also showed that substitution had taken place in the amino group of the amine molecule, thus indicating the presence of a free carbonyl group in the original molecule. Phelps obtained a yellow dyestuff by treating the liquor with nitric acid. He failed to learn the structure of this body. It was found that the dyestuff could not be manufactured economically.

Perhaps the most promising method for utilizing the liquor is that of the production of alcohol from it. This is being carried out to a considerable extent in Sweden. It has been calculated that nearly two per cent. of the organic material of the liquor is fermentable by yeast. The process consists essentially as follows: The acid of the liquor is nearly neutralized with lime, the liquor is then aerated, and the lime sludge, consisting of calcium sulphate and part of the organic matter, is removed. The clear liquid is now treated with a special yeast cultivated for the purpose, and a weak current of air is blown through the liquid during the fermenting period. The fermentation is completed after four to six days. Upon distillation 1.2 volumes per cent. of alcohol is obtained. The raw alcohol contains cymol, methyl alcohol, acetone, and acetaldehyde as impurities. There is considerable doubt in regard to the market for the large amount of such a grade of alcohol that could be made from such a tremendous supply of raw material. Further, since only about two per cent. of the organic material is utilized, the process does not completely solve the problem of its disposal.

In spite of the fact that a tremendous amount of work has been done on the subject, the problem still remains for the most part unsolved. It is to be noted that most of the investigation work that has been carried on in the past has not been for the purpose of determining the actual structural relations existing in the molecule of the main constituent of the organic substance of the waste liquor. This accounts, no doubt, for the meagre knowledge we possess of this substance. We can scarcely hope to make much advancement in the utilization of this substance until we know more about its composition. What we need is more purely scientific investigation into the structure of the main organic substance. It is true that such an investigation is beset with great difficulties owing to the inertness of the substance towards solvents. Attempts seem to be made toward recovery of the sulphur (on the understanding that it is in the form of a sulphonic group).

At present this seems to be a chemical impossibility. If such could be accomplished, however, the cost of the production of pulp would be considerably reduced. The work on the amine condensation products should be extended with the purpose of solving their structure, as well as for working up useful substances from them.

Further work might be done to try to increase the amount of fermentable material for the production of alcohol. The subject of its use in the treatment of roads should be investigated more fully and on existing roads.

GREATEST USER OF ASBESTOS.

If the United States can not boast of pre-eminence in asbestos production, as it can for many other minerals, it is at least a matter of some gratification to know that the bulk of the world's production comes from America and that the Canadian deposits yield by far the larger part of the total. In this, too, the United States benefits, for the nearness and reliability of the Canadian supply, largely owned in the United States, afford the basis for our evental unquestioned supremacy in the development of asbestos manufactures. Even as it is, there are, according to J. S. Diller of the United States Geological Survey, some valuable deposits and promising prospects in the United States and these would undoubtedly be much more largely developed were it not for the extent of the Canadian deposits. The domestic production in 1912, according to Mr. Diller, was 4,403 short tons, valued at $87,959, and although this was a decline of 42 per cent in tonnage compared with the output for 1911, it was only 27 per cent less in value, owing to the larger quantity of higher-grade asbestos in 1912. Georgia, Vermont, and Wyoming are the three States which mine asbestos. The Canadian exports of asbestos in 1912 amounted to 88,008 tons, of which 71,426 tons, or more than 81 per cent, was imported into the United States. This quantity was 67 per cent of the entire Canadian production.

Asbestos is the most important fireproofing material known. Its fibrous structure adapts it to a wide range of applications—from woven fabrics, such as theater curtains and articles of clothing, to asbestos shingles, stucco, plaster, asbestos "wood," and various other forms of building material that render structures thoroughly fireproof.

THE ELECTRODEPOSITION OF TIN.*

By EDWARD F. KERN.

This paper is a compilation of data collected from all the available literature and contributed to the Symposium on the Electrodisposition of Metals, in accordance with the request of the President of this Society.

Tin is largely used as a protective coating to articles of iron, steel, copper, brass and bronze. The process of coating large articles of iron, steel and copper by merely bringing their cleaned surfaces in contact with molten tin and then removing the excess either by means of rolls or by centrifugal machines, is so much cheaper than electrolytic methods and moreover gives such sound and perfect coatings, that the electrodeposition methods have found little application except for coating small articles and those which have an irregular surface.

A great amount of electrodeposition of tin is done for the coating of small articles such as pins, hooks, eyes, screws, clasps, etc., for which purpose this method is preferable. Another application of electrodeposition is that of giving a preliminary coating to iron or steel, which is subsequently to receive an electrodeposit of a metal which is more electropositive than iron.

The consideration of electrolytes, as given below, was done in the following order under each of the headings: A—Acid Electrolytes, B—Neutral Electrolytes, C—Alkaline Electrolytes.

I. ELECTRODEPOSITION OF TIN BY IMMERSION.

The use of the immersion process of tinning is principally for coating small articles of copper, brass and iron, such as hooks, eyes, pins, buttons, clasps, screws, etc., with a thin, bright, adherent deposit of tin. The immersion method consists in placing the articles in contact with either metallic tin or zinc in a boiling solution of a tin salt or a solution containing a tin salt and one or more salts.

1. One of the most generally used immersion baths is a saturated solution of cream of tartar (potassium hydrogen tartrate) to which has been added from 15 to 30 grams of tin chloride per liter. Boil and place the articles in the boiling solution and stir with a rod of metallic tin (Barclay and Hainsworth, "Electroplating," 1912 Ed., p. 333; Fields, "Principles of Electroplating," 1912 Ed., p. 221). Instead of using a rod of tin to stir the solution the articles may be placed in alternate layers with granulated or sheet tin, which will cause the articles to be coated with a white, smooth, adherent deposit of tin (Fields, "Principles of Electroplating," 1912 Ed., p. 211). If the metallic tin be replaced by metallic zinc, and stannous chloride added to the solution from time to time, thicker deposits of tin on the articles may be obtained and in a shorter time. In this case no tin is being added to the solution to replace that which is deposited on the articles, so it will be necessary to reject the solution when much zinc has accumulated in it. (Fields, "Principles of Electroplating," 1912 Ed., p. 211; Barclay and Hainsworth, "Electroplating," 1912 Ed., p. 333; Metal Industry, 4, 225 (1906).) The articles, after proper coating has been obtained, should be rinsed in water, dried by shaking with sawdust, and polished with a scratch brush or by rolling in a polishing barrel.

2. An immersion solution which has given satisfaction for coating iron and steel articles with tin was used by Roseleur. It is prepared by dissolving 20 to 30 grams of ammonium alum and 1 to 2 grams of anhydrous tin chloride per liter of water. (Barclay and Hainsworth, "Electroplating," 1912 Ed., p. 333; Brass World, 8, 180 (1912).) Potash alum does not give good results. Fused tin chloride is used because it does not contain any free acid, which will cause the coating to peel. The solution must be used boiling, and the iron articles must be clean of rust and grease, which are removed by an "alkali dip" and by a pickling solution. A bright coating of tin will be produced within 30 to 60 seconds. The solution must be replenished with tin from time to time by adding fused tin chloride in the original proportion to the volume of solution. As iron stands above tin in the E. M. F. series, the iron replaces an equivalent of tin in the solution, so when iron has accumulated to an amount which causes the coating to deposit in non-adherent form the solution must be rejected.

3. The solution devised by Elsner for coating copper and brass articles, and which gives reliable results (Barclay and Hainsworth, "Electroplating," 1912 Ed., p. 333) is prepared by dissolving 2 grains of sodium chloride and 2 grains of stannous chloride in one liter of water. It is used in the same manner as solution 1.

II. ELECTROLYTIC DETERMINATION OF TIN.

Tin may be quantitatively precipitated from certain solutions by electrolyzing them under such conditions of temperature, composition or solution, and current density, as have been found to give accurate results. The solutions which give the most satisfactory results are in most cases those which contain the tin either as ammonium sulpho-stannate.

1. Smith states that tin may be quantitatively deposited from a solution which contains ammonium oxalate. (Smith's "Electro-analyses," 1911 Ed., p. 169; Neumann-Kershaw, "Electrolytic Methods of Analysis," 1898 Ed., p. 149). Potassium oxalate is not advisable, as a basic salt of tin is liable to separate upon the anode. The conditions which were found to give good results are: The solution, 125 to 150 c.c. in volume, containing about 0.5 gram of tin as chloride and about 4 grams of ammonium oxalate, is acidified with 9 to 10 grams of oxalic acid (acetic acid may be used instead of oxalic acid), heated to about 65° C. and electrolyzed at C. D. of 1 to 1.5 ampere per sq.

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decimeter. Deposits formed under these conditions are bright and adherent.

2. Classen found that dense, bright, adherent deposits could be quantitatively formed in an acid ammonium oxalate solution. He added 120 c.c of a saturated solution of ammonium oxalate to 25 c.c solution containing 0.9 to 1.0 gram of stannic ammonium chloride, then electrolyzed at 30 to 35° C. with current of 0.3 to 0.6 ampere and voltage at 2.8 to 3.8. Acid ammonium oxalate must be added at intervals if a larger quantity of tin is to be deposited. Time required was about 9 hours for complete precipitation. The tin separated as a brilliant, white, adherent deposit. It was washed, dried and weighed in usual way. (Smith's "Electro-analysis," 1911 Ed., p. 169; Neumann-Kershaw, "Electric Methods of Analysis," 1898 Ed., p. 149).

In case the tin is to be determined in a solution containing it as potassium sulpho-stannate, Classen recommends that it be converted into the oxalate, and then electrolyze. This is accomplished by acidifying the solution with hydrochloric acid, then boiling off the hydrogen sulphide, and adding hydrogen peroxide to oxidize the tin to metastannic acid, which is a white precipitate. Add a few c.c of sulphuric acid, neutralize with ammonia, and again add hydrogen peroxide. Filter out the metastannic acid, wash, dissolve in a solution of oxalic acid and ammonium oxalate, and electrolyze under conditions given above. Use ordinary platinum electrodes.

3. C. Engel gave the following conditions for quantitatively depositing tin by electrolysis as a bright, white, smooth, adherent deposit: Add to the solution, containing about 1 gram of tin as ammonium stannic chloride, a few c.c of oxalic acid solution to clear the turbidity, then add 0.3 to 0.5 gram of hydroxylamine hydrochloride or sulphate, 2 grams ammonium acetate, and 2 grams tartaric acid. Dilute to 150 c.c heat to 60 to 70° C. and electrolyze at C. D. of 0.9 to 1.0 ampere per sq. dm. and potential of 4 to 5 volts. (Journal Society Chemical Industry, 15, 219; Neumann-Kershaw, "Electrolytic Methods of Analysis," 1898 Ed., p. 151; Smith's "Electro-analysis," 1911 Ed., p. 171).

4. Campbell and Champion determined tin in ores by fusing 1.0 gram of the finely ground sample with 5 to 6 grams of a mixture of equal parts of sodium hydroxide and sulphur for 1½ hours at red heat in a porcelain crucible. The fusion was then digested with 40 to 50 c.c of hot water, the solution filtered, and the residue washed and discarded. The filtrate was acidified with hydrochloric acid, which precipitated the tin as stannic sulphide, boiled off the hydrogen sulphide, added 10 c.c concentrated hydrochloric acid and gradually introduced 2 to 3 grams of sodium peroxide until a clear solution was obtained. Boiled about 3 minutes, then filtered out the separated sulphur and washed. Added ammonia to the filtrate to permanent precipitation, and then 50 c.c of a 10 per cent acid ammonium oxalate solution. Electrolyzed over night at C. D. of 0.1 ampere per sq. dm. and about 4 volts. Deposit of light color and very adherent. (Neumann-Kershaw, "Electrolytic Methods of Analysis," 1898 Ed., p. 150).

In the course of any analysis, when tin is obtained as sulphide, the electrolytic determination may be conducted by getting the precipitate into solution as chloride by digesting it at boiling with 10 c.c of concentrated hydrochloric acid and 70 c.c of water to which is gradually added 2 to 3 grams of sodium peroxide. Then proceed in same manner as given above. (Journal Society of Chemical Industry, 17, 1073.)

5. Pasztor rapidly and quantitatively deposited tin from tartaric acid solutions which contained from 4 to 6 grams of tartaric acid, 2 to 6 grams of ammonium acetate, and 1 to 1½ grams of hydroxylamine hydrochloride or sulphate per 150 c.c volume, Electrolyzed at 60 to 80° C. at C. D. of 0.8 to 1 ampere per sq dm.

Pasztor also stated that stannous sulphide dissolved in hot hydrochloric acid solution containing ammonium chloride gave a clear solution from which the tin was quantitatively deposited. (Electrochem. Zeitschrift, 16, 281; Smith's "Electro-analysis," 1911 Ed., p. 171; Neumann-Kershaw, "Electrolytic Methods of Analysis," 1898 Ed., p. 151; Arrhenius, "Textbook of Electro-chemistry," p. 274.)

6. Classen discovered that a dilute solution of tin containing an excess of ammonium sulphide would yield a quantitative deposit of the metal, but that the deposits formed in a sodium or potassium sulphide solution were dark gray and non-adherent. (Smith's "Electro-analysis," 1911 Ed., p. 170; Neumann-Kershaw, "Electrolytic Methods of Analysis," 1898 Ed., p. 150.) The conditions for obtaining a satisfactory deposit of tin from ammonium sulphide solution containing the tin as ammonium sulpho-stannate are: 150 c.c solution containing an excess of ammonium sulphide, heated at 50 to 60° C., and electrolyzed at C. D. of 1 to 1½ ampere per sq. dm. and potential of 4 to 5 volts. (Arrhenius, "Textbook of Electro-chemistry," p. 274.)

Use of Rotating Electrodes.—The use of rotating anodes, revolved at 300 to 500 times per minute, enables the quantitative precipitation of tin to be made from ammonium oxalate solutions and ammonium sulphide solutions in 20 to 30 minutes, giving a deposit like polished silver. The electrolysis is conducted with C. D. of 5 to 8 amperes per sq. dm. and E. M. F. of 5 to 8 volts. (Smith's "Electro-analysis," 1911 Ed., p. 172.)

Removal of Tin Deposits from the Cathode.—The deposit of tin on the platinum cathode may be readily removed by fusing with potassium bisulphate, or dissolving in a mixture of nitric acid and oxalic acid, or by means of dilute hydrochloric acid with a piece of metallic zinc in contact with the cathode. (Smith's "Electro-analysis," 1911 Ed., p. 169.)

III. ELECTRODEPOSITION OF TIN BY SEPARATE CURRENT.

On account of the whiteness of tin and it not becoming tarnished by exposure to the atmosphere, an electrolytic deposit of this metal is much desired. There are many uses which could be made of small metallic articles which are coated with an adherent, smooth, dense, bright deposit of tin, but the difficulty of obtaining such a deposit has hindered the larger practice of electroplating with tin.

A number of electrolytes have been suggested, some of which have been patented, but the choice of the propr solution for the coating of articles of iron, steel, copper, brass or bronze will in most cases largely depend upon the character of the work to be done, and the available conditions, such as the source and quantity of current, means of controlling the temperature of the electrolyte, size of the articles, and the method of handling and treating them before and after the electrolysis has been conducted.

The electrolytes which are given below are those which have been recommended and used for electroplating of tin. In many cases the published composition of the electrolytes was given in either ounces or pounds of the ingredients per gallon, but in order to allow ease of comparison of the different solutions, their compositions were calculated into grams per liter, and temperatures were changed from Fahrenheit into Centigrade.

1. Good deposits of tin may be produced by using an electrolyte containing stannous chloride and acid ammonium oxalate. One liter of this solution is prepared by dissolving 25 to 30 gms. of crystallized stannous chloride in about 400 cc. of water, 55 to 65 gms. of ammonium oxalate and 3 to 4 gms. of oxalic acid in about 400 cc. of water. Add the oxalate solution to the tin solution with vigorous stirring, so that the white precipitate which forms at first will dissolve. Dilute 1 liter and boil a few minutes. The deposits formed from this electrolyte are said to be excellent, and, further, the anodes corrode normally, so there is no need of adding tin salt to the electrolyte from time to time. This solution has the advantage that it can be mixed with a similarly prepared copper solution, and the mixed solution used for depositing a coating of bronze. (Barclay and Hainsworth, "Electroplating," 1912 Ed., p. 331. Field's "Principles of Electroplating," 1911 Ed., p. 213.)

2. Roseleur's tin bath is recommended as giving the most satisfactory deposits of any of the generally-used electrolytes. It is prepared by dissolving 10 to 12.5 gms. of sodium pyro-phosphate in 1 liter of water and suspending 1 to 1.5 gms. of fused stannous chloride in the solution by placing it in a copper screen or in a linen bag. Agitate till all the tin chloride is dissolved. The solution is at first cloudy, but finally becomes clear and is ready for use. Voltage required from 1.5 to 4 volts. Use pure tin anodes.

It is stated that any metal may be coated with tin in this solution, the deposit having a dead-white lustre resembling silver, which may be polished by either scratch-brushing or by burnishing. Articles of zinc, copper, brass and bronze may be directly tinned in this bath, but those of iron and steel must be first tinned in an immersion solution (See I, 2) or else electro-coppered then scratch-brushed and finally placed in the tin bath. (McMillian-Cooper, "Electrometallurgy," 1910 Ed., p. 248; Barclay and Hainsworth, "Electroplating," 1912 Ed., p. 331; Watt and Philip, "Electroplating and Electrorefining," 1911 Ed., p. 344; Langbein-Brannt, "Electrodeposition of Metals," 1909 Ed., p. 439.)

The Roseleur electrolyte is the one most generally used for electro-tinning. It is capable of giving the whitest deposit of any of the tinning baths which are in general use. The objections to it are that it must be worked hot, that heavy deposits cannot be obtained except after a period of several hours, and that the anodes do not dissolve normally, which necessitates that a concentrated solution of tin chloride be added to the working solution from time to time.

The Roseleur bath has been modified in concentration by other electroplaters: Weiss used a solution containing 1 gm. of fused stannous chloride and 5 gms. of sodium pyrophosphate per liter. (McMillian-Cooper, "Electrometallurgy," 1910 Ed., p. 249.) A solution recommended as giving excellent results is prepared by dissolving 15 gms. of sodium phosphate crystals in 1 liter of water, and adding 7.5 gms. tin chloride. Work at low current density. (Metal Industry, 4, 138 (1906).) Another solution, said to have been recommended by eminent authorities, contains 37 gms. sodium phosphate crystals and 20 gms. fused tin chloride per liter. The tension required for this electrolyte was given as 1 to 1.5 volt, when worked hot. (Metal Industry, 5, 376 (1907).)

3. An electrolyte which gives good results when electrolyzed at ordinary temperature is prepared by dissolving 15 gms. of ammonium chloride and 30 gms. of fused stannous chloride in a liter of water. Use pure tin anodes, and regulate the current so as to avoid pulverulent deposits. (Metal Industry, 9, 519 (1911).)

4. An electrolyte which is strongly recommended as giving excellent results is prepared by dissolving 45 gms. of diammonium stannic chloride per liter of water. Electrolyze at tension of about 1.5 volt. (Metal Industry, 5, 376 (1907).)

5. A good, lustrous deposit of tin may be produced by using an electrolyte prepared by dissolving 30 to 60 gms. of cream of tartar (potassium hydrogen tartrate) in a liter of water, and adding 7.5 to 15 gms. of tin chloride crystals. Use pure tin anodes, and electrolyze at temperature not less than 70° C. at E. M. F. of 3 to 5 volts. A good lustrous deposit can be obtained in to 20 to 30 minutes; scratch-brush with a soft steel brush, or polish on a soft buff-wheel using Vienna lime and kerosene. Keep the solution

between 5 and 6° B. (Metal Industry, 6, 162, 227 (1008); 7, 227 (1909).)

6. A solution which has been used considerably for tinning articles of iron, steel and brass is prepared by dissolving 60 gms. of caustic soda in about 800 cc. of water, and 22.5 gms. of fused stannous chloride in small amount of water, then pour the tin solution into the caustic solution and dilute to 1 liter. Electrolyze cold, using pure tin anodes, and potential of 1 to 1.5 volt (Bedell's "Practical Electroplating," 1909 Ed., p. 143). If the solution becomes impoverished in tin it should be revived by adding fused stannous chloride. If solution assumes a milky appearance, add caustic soda until it clears. Keep at about 11° B.

While the work is being plated it takes on a frosty appearance which is usually porous; the work should then be removed from the bath and scratch-brushed. This may have to be repeated several times, if thick deposits are desired. When mechanical plating-barrels are used scratch-brushing will not be necessary, as the rolling and the rubbing of the articles cause them to become burnished. Articles of iron and steel must first be given a slight coating of copper in a copper cyanide electrolyte, preferably hot.

7. A tin bath which has given satisfaction is prepared by dissolving 12 gms. of metallic tin in hydrochloric acid, evaporating to expel the free acid, then adding to a solution of 25 gms. of potassium hydroxide, and diluting to 1 liter. The addition of stannous chloride must be made from time to time as needed. (Barclay and Hainsworth, "Electroplating," 1912 Ed., p. 330.)

8. Elsner used an alkaline eletrolyte which he recommends as having given satisfaction for electro-tinning iron and steel. It was prepared by adding 25 gms. of tin tetrachloride to 1,000 cc. of water and adding sufficient caustic potash to give a clear solution. He used cast tin anodes, and required a potential of 3 to 5 volts. (McMillian-Cooper, "Electrometallurgy," 1910 Ed., p. 248.)

9. Hearn prepared an electrolyte which he used for general work by dissolving 21 gms. of tartaric acid and 30 gms. of caustic soda in 1 liter of water, then adding 3 gms. of fused tin bichloride. (McMillian-Cooper, "Electrometallurgy," 1910 Ed., p. 249.)

10. Fearn recommends a bath which he prepared by disssolving 25 gms. of tartaric acid in about 400 cc. water, 75 gms. of caustic potash in about 400 cc. water, and 1.3 gm. of fused stannous chloride in 50 cc. of water. The caustic solution was added to the tin solution, then the tartaric acid solution mixed with it. Diluted to 1 liter, and electrolyzed cold or hot. Thick bright deposit. (McMillian-Cooper, "Electrometallurgy," 1910 Ed., p. 249.)

11. Steele prepared an electro-tinning solution by dissolving 5.5 gms. of caustic potash, 16.5 gms. of potassium carbonate, and 66 gms. of sodium carbonate in 1 liter of water, after which he added 17.5 gms. of tin dioxide, 1 gm. potassium cyanide and 1 gm. zinc acetate. Filtered before using. (McMillian-Cooper, "Electrometallurgy," 1910 Ed., p. 249; Watt and Phillip, "Electroplating and Electrorefining of Metals," 1911 Ed., p. 345.)

12. An alkaline bath proposed by Elsner for tinning iron and steel articles is prepared by putting 11 grams of tin bichloride in 1 liter of water, then adding a solution of potash lye of 10° B. until the precipitate is dissolved, and 10 gms. of potassium cyanide. (Langbein-Brannt, "Electrodeposition of Metals," 1909 Ed., p. 440.)

13. Good deposits of tin may be produced by dissolving 1.5 gms. of fused stannous chloride, 80 gms. of potassium carbonate, and 1 gm. of potassium cyanide, separately in water; then adding the cyanide solution to the tin solution and finally stirring in the carbonate solution. Dilute to 1 liter. This solution is not a very good conductor of current, thus requiring a high voltage; still satisfactory deposits may be obtained. (Barclay and Hainsworth, "Electroplating," 1912 Ed., p. 331.)

14. Salzedes used a bath for tinning iron which he prepared by adding 10 gms. of potassium cyanide, 110 gms. of potassium carbonate, and 2.5 gms. of stannous chloride to 1 liter of water. By electrolyzing with voltage at 4 to 5, a heavy dense deposit was rapidly obtained. (Langbein-Brannt, "Electrodeposition of Metals," 1909 Ed., p. 441.)

15. An electrolyte patented by Fearn in 1873 contained 1.2 gms. of fused tin bichloride, 111 gms. caustic potash, 111 gms. potassium cyanide, and 111 gms. of sodium pyrophosphate per liter. Each of these chemicals were separately dissolved in water; the tin solution was poured into the potash solution with constant stirring, then the cyanide solution was added, and finally the pyrophosphate solution. Electrolyzed at ordinary temperature. Bright thick deposits were obtained. It was found necessary to add fused tin chloride to the bath from time to time, as the anodes were not dissolved as rapidly as the tin deposited. (Watt and Phillip, "Electroplating and Electrorefining of Metals," 1911 Ed., p. 345; McMillian-Cooper, "Electrometallurgy," 1910 Ed., p. 248.)

16. The following solutions are capable of giving good white deposits upon all metals, and may be used cold:

(a) Solution for electro-tinning brass, bronze and copper; 7.5 gms. of caustic potash, 7.5 gms. of stannous chloride, and 35 gms. of potassium cyanide per liter.

(b) Solution for steel, wrought iron and cast iron; 15 gms. of caustic potash, 15 gms. of stannous chloride, and 35 gms. of potassium cyanide per liter. Dissolve the caustic potash in water, add the tin chloride, then the potassium cyanide. If the tin chloride contains any iron, a precipitate will remain suspended in the solution, which should be filtered off. These solutions may be used either cold or hot.

Better deposits are formed in the warm solutions. Use as large anode surface as possible and electrolyze at tension of 2.5 to 3 volts. (Brass World, 7, 121 (1911).)

A more concentrated caustic solution than the above is said to have given very satisfactory deposits. It contained 60 gms. of soda lye, 45 gms. of fused stannous chloride, and 12 gms. of potassium cyanide per liter. Electrolyzed at 1.5 volt. (Metal Industry, 5, 376 (1907).)

17. J. C. Beneker obtained U. S. Patent 921,943, assigned to the Meaker Company of Chicago, for a tin electrolyte, the composition of which is 125 gms. of sodium hydroxide, 75 gms. of sodium thiosulphate, and 50 gms. of crystallized stannous chloride per liter. The solution is prepared by dissolving each of the salts separately, mixing the stannous chloride solution with the hydroxide solution, then adding the thiosulphate solution. It is stated that possibly the chief constituent of the prepared solution is sodium thiostannate (Na_2SnS). By using pure tin anodes, the deposit is produced without the formation of sponge or tree-like crystals, even when operated at high current density. The electrolyte may be used either cold or hot, but preferably hot. (Electrochemical and Metallurgical Industry, 8, 285 (1909).)

18. An electrolyte of composition similar to the Beneker solution contains 120 gms. of sodium hydroxide, 60 gms. of sodium hyposulphite, and 30 gms. of chloride of tin per liter. (Metal Industry, 9, 90 (1911).)

19. An electrolyte which is recommended to give excellent deposits of tin is prepared to contain 90 gms. of caustic soda, 15 gms. of sodium hyposulphite, 15 gms. of sodium chloride and 30 gms. of tin chloride crystals per liter. This solution may be used either cold or hot, but gives better results when hot. Use anodes of pure tin. (Metal Industry, 8, 87 (1910).)

Conditions Necessary to Obtain Bright, Dense, Adherent Deposits of Tin.—The articles to be electroplated in any of these solutions must be carefully cleaned in a strong potash solution, then rubbed with lime and subsequently thoroughly washed in clean water before placing them in the electrolyte. No time should be lost in getting the articles immersed in the plating solution directly after washing. (McMillian-Cooper, "Electrometallurgy," 1910 Ed., p. 249.)

There is one drawback in depositing tin from most of the baths which are in general use, namely, the anodes are not dissolved in the same ratio as tin is deposited on the cathode, consequently the strength of the bath must be kept up by the addition of a tin salt. This is best accomplished by allowing a concentrated solution of the tin salt to drip constantly into the bath during the time it is working. (Watt and Phillip, "Electroplating and Electrorefining," 1911 Ed., p. 342.)

Tin baths should not be used at temperatures below 20° C.; as a general rule, the higher the temperature the better the deposit.

Too high current density causes a spongy deposit, which does not adhere; whereas, with a suitable current density, a dense, reguline deposit will be obtained. (Langbein-Brannt, "Electrodeposition of Metals," 1909 Ed., p. 441.)

W. Pfanhauser conducted a number of experiments on the formation of spongy and crystalline deposits of tin by electrolysis. He stated that the electroprecipitation of tin as thick adherent deposits is possible only in very concentrated tin-salt electrolytes, and those which contain no cations which will give rise to strongly dissociated solutions about the cathode. The best conditions for good tin deposits were found to be circulation of electrolyte, low current density, and high concentration of tin in the electrolyte. Spongy deposition is caused by poor circulation, dilute solutions, high current density, acid solutions, and impure solutions. Crystalline deposits form when the electrolyte contains no cations which are capable of forming alkali hydroxides or similar compounds, which are accompanied by the liberation of hydrogen. He used Roseleur's solution of tin chloride and sodium phosphate, and concentrated solutions of tin tetrachloride and stannous chloride. (Zeitschrift für Electrochemie," 8, 41 (1902); Electrochemist and Metallurgist, 2, 42 (1902); Journal of Society of Chemical Industry, 21, 261 (1902).)

In an article in "The Electrolytic Preparation of Tin Paste," the statement was made that "A spongy deposit may be due to various causes, but may be obtained nearly always by using too high a current density at the cathode. This results in an impoverishment of the electrolyte near the cathode with respect to the ions of the metal to be deposited, so that some other metal, and also generally hydrogen, is simultaneously deposited. It is under such conditions that the metal deposit becomes spongy." (Electrochemical and Metallurgical Industry, 3, 59 (1905).)

IV. ELECTROLYTIC REFINING OF TIN.

On account of the ease and comparative cheapness of refining tin by liquation methods (M. P. of tin = 232°C.) and by oxidation methods, electrolytic refining has little promise of being commercially employed.

Practically the only ore of tin is cassiterite (SnO_2; Sp. Gr. = 6.8 to 7.1; when pure it contains 78 per cent tin), which is found associated with such minerals as quartz, feldspar, and mica in the form of granite or gneiss gangue. In some localities cassiterite is also accompanied by metalliferous minerals such as pyrite, arsenopyrite, chalcopyrite, wolframite and molybdenite. These minerals, with the exception of wolframite, may be separated by water concentration methods. A recently developed method for separating wolframite, in case pyrite is also present, consists in calcining to the magnetic condition, then subjecting the pulverized ore to magnetic separation, the pyrite and the wolframite being removed. (Schnabel-Louis, "Handbook of Metallurgy," II, 1907 Ed., p. 478; Louis, "Metallurgy of Tin," 1911 Ed., p. 12.)

Commercial tin contains from 0.5 to 1.5 per cent of

impurity, which is one or more of the following metals: zinc, iron, lead, bismuth, antimony, copper, arsenic, tungsten, molybdenum, silver. As there is no demand for very pure tin, and also because silver and gold are not present in quantity to pay for their recovery, electrolytic refining has, up to the present time, not been practiced, except when very pure metal was wanted, or when experimental refining was conducted. The product which is produced by pyro-heat methods of refining is of sufficient purity for commercial purposes.

A number of electrolytic methods have been developed, the majority using electrolytes of the stannous salt. The efficiency of the refining is given for some of the electrolytes, the figures being obtained by using the factors for stannous solutions which are 0.6163 mgms. per coulomb, 2.2188 gms. per ampere-hour, 204.43 ampere-hours per pound; the factors for stannic solutions are 0.30817 mgms. per coulomb, 1.1094 gms. per ampere-hour, 408.86 ampere-hours per pound.

1. Brand conducted experiments on the electrolytic refining of tin, using an electrolyte containing 2.5 per cent by volume of concentrated hydrochloric acid and 9 per cent by weight of stannous chloride. The method did not find commercial application. (Schnabel-Louis, "Handbook of Metallurgy," 1907 Ed., II, p. 549; Dammer, Chem. Technology, ii, 27 and 324.)

2. Michaud and Delasson received French Patent 435,936 for the use of a tin electrolyte prepared by dissolving stannous chloride in water, adding sulphuric acid till the precipitated oxychloride dissolved, and then stirring into the solution about 1 per cent of magnesium chloride and 1 per cent of boric acid. The cell used for the refining is constructed with a sheet copper cathode placed horizontally on the bottom, on which the tin crystals are deposited and removed by scrapers. (Journal Society Chemical Industry, 31, 395 (1912).)

3. Mennicke conducted experiments on the electrolytic refining of tin in fluosilicate electrolytes, and obtained deposits which were similar to lead deposits produced under the same conditions of current-density and temperature. The electrolyte was prepared by dissolving freshly precipitated stannous hydroxide in hydro-fluosilicic acid in proper proportions to give a solution containing 10 per cent tin and 10 per cent free hydro-fluosilicic acid by weight. Tin oxide was found to be insoluble in hydro-fluosilicic acid. The presence of free hydro-fluoric acid was found not to interfere with the production of satisfactory deposits.

The electrolysis was conducted at 20° C., using current at density of 9.3 ampere per sq. ft. (1 amp. per sq. dm.) and an average of 0.4 volt. Distance between electrodes about 2 inches (5 cm.). The tin deposited extremely solid and tough, even without the presence of any addition-agent such as gelatine or albumen. The lower the voltage the finer the crystals.

Better results were obtained by using pure tin anodes than with those of a tin alloy. The presence of lead finally caused the deposit to become spongy, but still the deposited tin was pure. He states that very pure tin can be produced, which is especially suited for preparing pure chemicals. (Electrochemical Zeitschrift, 112, 135, 161 and 180 (1905); Zeitschrift für Electrochemie, 12, 112; Electrochemical and Metallurgical Industry, 4, 26; Mineral Industry, 14, 555; Betts, "Lead Refining by Electrolysis," 1908, p. 47.)

4. Mention has been made that neutral concentrated solutions of either stannic chloride or stannous chloride can be used for producing pure tin, as these electrolytes yield a coarse crystalline deposit. (Neumann-Kershaw, "Electrolytic Methods of Analysis," 1898 Ed., p. 148.)

5. Beautiful dense deposits of tin can be produced without the evolution of hydrogen at the cathode by electrolyzing a solution of sodium-stannous chloride with low current-density, and at ordinary temperature. (Bulletin Soc. d'Enc. L'Ind. Nat., July, 1912, p. 28.)

6. Quintaine was granted English Patent 5,496 for the deposition of pure tin by use of an electrolyte composed of stannic chloride, or stannous chloride, and an ammoniacal salt, preferably ammonium chloride. It is claimed that a perfect deposit of chemically pure tin was produced from this solution. The statement is made that "to obtain a clear solution, and one that will act as a good conductor of the current, the precipitate first formed on dissolving the tin salt in water is redissolved by the addition of ammonium chloride, and the solution filtered. The current should be weaker than that employed for the electrodeposition of copper, or the deposit will be irregular." (Journal Society Chemical Industry, 19, 1121 (1900); Mineral Industry, 9, 646).

7. Hollard prevented the formation of spongy deposits of tin by using an electrolyte composed of 12 gms. of sodium stannate (Na_2SnO_3) and 200 gms. of sodium sulphate per liter, and electrolyzing it at a temperature of 80° C. at current-density of 2 amperes per sq. ft. (0.2 ampere per sq. dm.) (Bulletin Soc. d'Enc. L'Ind. Nat., July, 1912, p. 28.)

8 Fischer satisfactorily deposited tin by using a solution of ammonium sulpho-stannate to which was added a reducing agent such a sodium sulphite, sodium hyposulphite, or potassium cyanide. (Zeitschrift Anorg. Chemie, 42, 363 (1904).)

9. Neumann received German Patent 198,289 for a process of obtaining pure dense deposits of tin by use of an electrolyte composed of an alkali sulpho-stannate, and operating at temperature of about 70° C. The presence of free alkali is said to be advantageous.

10. Claus refined tin in an aqueous solution of sodium sulpho-stannate, of sp. gr. 1.07, and at 90° C., employing current at 10 amperes per sq. ft. (0.9 amp. per sq. dm.). All the impurities except arsenic and antimony collected as anode sludge, principally as sulphides. Arsenic and antimony, when present, were

precipitated on the cathode with the tin. He found that the cathode tin containing arsenic and antimony could be freed from these by making it an anode in an acid solution of sodium thiosulphate containing hydrochloric acid, the arsenic and antimony in this case remaining as sulphides in the anode sludge. The cathode tin was melted and cast into bars. (Electrochem. Zeitschrift, 8, 168; Schanbel-Louis, "Handbook of Metallurgy," 1907 Ed., 11, 549.)

11. Patents have been granted to O. Steiner for a tin refining process, using an electrolyte similar to that published by Claus, as given above (10). The patents issued are: U. S. Patent 890,249; German Patent 193,528, English Patent 10,230, French Patent 374,116. The claims are that by using an electrolyte containing about 10 per cent by weight of an alkali sulphide, to which has been added about 1 per cent by weight of flowers of sulphur, tin of high purity (99.9 per cent) could be produced as a dense smooth deposit, when the electrolysis is conducted so that the E. M. F. is kept below 0.2 volt, current-density under 4.5 amperes per sq. ft., and solution kept at about 90° C.

The electrolyte is prepared by dissolving commercial sodium sulphide in the necessary amount of water to produce a 10 per cent solution, adding 1 per cent by weight of flowers of sulphur, letting settle, then filtering. It is necessary to analyze the solution at intervals during the electrolysis, and to add sodium sulphide and flowers of sulphur so as to keep up the concentration. The loss of sodium sulphide will be due to oxidation and to the formation of sodium sulphostannate. The amount of tin in the electrolyte reaches a maximum of about 2.2 per cent by weight, and remains constant thereafter so long as the concentration of sodium sulphide is kept proper.

One of the essentials in the use of this solution for refining tin is that the voltage must be kept below 0.2, and that the electrolyte be maintained above 90° C. If the potential is allowed to rise, gassing at the cathode occurs. At 0.6 volt violent liberation of hydrogen takes place, with decomposition of the electrolyte and at the same time the tin deposits as a dull spongy mass, which contains oxide.

The raw tin should not contain more than 10 per cent of impurities, and the iron content should be below 2 per cent, otherwise the anode sludge will adhere and cause the voltage to rise and produce gassing and a spongy deposit. The anode sludge will contain the iron, lead, antimony, copper, bismuth and silver. Distance between the electrodes about 1⅜ in. (3.5 cm.). Iron tanks are most suitable.

The conditions which are given as being necessary to obtain high current efficiency and to produce dense, pure deposits are:

a. Temperature of electrolyte above 90° C.

b. Thorough and constant circulation, or mixing of electrolyte.

c. Voltage maintained below 0.2.

d. Pure plate cathodes (cathodes of iron, copper and lead cause the voltage to rise and the deposit to be non-adherent and spongy).

e. Pure electrolytes, free of arsenic, antimony, copper, etc.

f. Electrolyte containing 10 or more per cent of sodium sulphide by weight. A more concentrated solution permits the use of higher current-density.

g. Add to the electrolyte about 1 per cent by weight of flowers of sulphur just before placing a new lot of anodes in the tank. The sulphur is necessary to form sulphides with the impurities in the anode, thereby preventing the contamination of the electrolyte.

h. The electrolysis must not be interrupted until the anodes are to be removed. When the current is interrupted, gassing will occur when the current is switched on, and spongy deposit will form.

A means of maintaining the same current-density from a number of electrodes when placed in the same tank, was accomplished by soldering all of the anodes to the same supply conductor, and all of the cathodes to the negative conductor. When this was not done the voltage between all of the opposite electrodes was not the same.

The ampere-hour efficiency is given as above, 98.5 per cent. It is also stated that "the deposit could be still improved by adding a colloid to the electrolyte, for example, gelatine as is used in the Betts' process for electrolytically refining lead." (Electrochem. Zeitschrift, May, 1908; Journal Society Chemical Industry, 26, 768 (1907); Electrochemical and Metallurgical Industry, 5, 309 (1907).)

12. Sperry obtained U. S. Patent 874,707 for a process of refining tin by the use of a diaphragm cell. It is stated that electrolytes consisting either of sulphate, ammonium oxalate, ammonium sulphide, or of chloride, fluoride, or hydrofluoric acid could be used in the cell. The impure metal to be electrolytically refined may be given a preliminary refining by fire-methods in order to remove the major portion of the impurities, then cast into anodes. The use of the diaphragm between the anodes and the cathodes is to prevent the cathode deposit becoming contaminated by floating anode sludge. The impurities which accumulate in the electrolyte as soluble salts are to be removed periodically by withdrawal of a portion of the electrolyte, and replacing it by fresh solution. Electrolytes work better when kept at 85° C. (Journal Society Chemical Industry, 27, 343; Electrochemical and Metallurgical Industry, 6, 76).

There are several articles, in themselves reviews, which could not be reviewed. They may be found in the following publications:

"Electrical Engineering," London, July 15, 1898. "The Electrolytic Refining of Tin and Recovery of Tin from its Ores," by Sherard Cowper-Coles.

"Electrochem. Zeitschrift," Berlin, March, 1907. "Recent Progress in the Metallurgy of Tin, with Regard to Electrochemistry in 1906," by H. Mennicke.

"Electrochem. Zeitschrift," Berlin, July, 1908. "Progress in the Metallurgy of Tin with Special Reference to Electrochemistry in 1907," by H. Mennicke.

"Electrochem. Zeitschrift," Berlin, January, 1910. "Electrolytic Precipitation of Tin," by B. Pasztor.

V. EFFECT OF ORGANIC ADDITION-AGENTS IN TIN ELECTROLYTES.

There should be little difficulty in obtaining thin, smooth, adherent deposits of tin; but when the deposition is carried to an appreciable thickness, difficulties arise. The electrodeposits of tin have a tendency to become crystalline and brittle, more and more so the longer the electrolysis is continued. (Barclay and Hainsworth, "Electroplating," 1912 Ed., p. 333.)

The physical condition of electrolytically deposited metals is economically of the most importance, since the metallurgist, as well as the electroplater, wants a coherent, dense, smooth deposit, as the purity of the cathode metal depends upon its density and smoothness; and, besides, the ampere-hour efficiency of a refinery is dependent upon the prevention of short circuits between anodes and cathodes. As a rule, the rougher the cathodes the lower the ampere-hour efficiency and the less pure the refined metal.

The characteristic form of tin, deposited from acid electrolytes, is a mass of loose, non-adherent crystals. This tendency is less apparent in neutral and in alkaline electrolytes. The concentration of the electrolyte, the temperature of the electrolyte, and the current-density, each have an effect on the character of the deposit. In general, the more concentrated the electrolyte up to saturation, and the higher its temperatures, the more coherent and smoother the deposit. Another factor influencing the deposition is one which is the result of the presence of certain organic addition-agents, which change the character of the deposit either beneficially or detrimentally.

The effect of addition-agents, when properly selected, is to cause the deposit to be smoother, denser, and more adherent. When not properly selected, the opposite effect will result—that is, the deposit will be more crystalline and less adherent, or collect as a spongy mass which drops from the cathode.

It has been found that the addition of glue or gelatine to certain tin baths, in the proportion of 1 part by weight to 1,000 parts of electrolyte, has a remarkable effect on the character of the deposited tin, and, at the same time, allows the use of a higher current-density. Other addition-agents which have been found to be beneficial for certain electrolytes are glucose, saccharine, acetone, and organic salts of aluminum and iron. The effect of organic addition-agents is not permanent, so in all cases, when used, further additions must be made periodically. (Barclay and Hainsworth, "Electroplating," 1912, Ed., p. 333; Fields, "Principles of Electrodeposition," 1911 Ed., p. 215.)

1. Hollis' U. S. Patent 916,155 is for the use of an electrolyte containing tin fluosilicate, and to which gelatine or glue is added for the purpose of increasing the density of the deposit. (Electrochemical and Metallurgical Industry, 7, 224 (1909).)

2. German Patent 244,567, to Matuschek, is for an electrolyte consisting of a concentrated solution of ammonium oxalate saturated with tin-ammonium chloride ($SnCl_2.2NH_4Cl$), to which an addition of black-oak tannin (quercitrinic acid) has been added. The electrolyte which he used was prepared by dissolving 200 gms. of stannous-ammonium chloride in 600 cc. of a concentrated solution of ammonium oxalate, then the addition of 50 gms. of black-oak bark tannin. This solution was electrolyzed at ordinary temperature, and a solid deposit of tin was produced, when current-density of 28 amperes per sq. ft. (3 amperes per sq. dm.) was employed. The statement is made that other additions may be made to the bath, such as sodium dihydrogen phosphate, sodium silicofluoride, an inorganic acid other than nitric acid, preferably hydrofluosilicic acid, or a mixture of borax and hydrofluosilicic acid. As an example of a bath of this composition, there was added, instead of 50 gms. of tannin, to the bath given above, 6 gms. of tannin and 6 gms. of sodium dihydrogen phosphate. This bath was found to be more constant than the first.

Claims were made that much higher current-density can be employed and the electrolysis be conducted at ordinary temperature, and the deposited tin still form solid and adherent, which is not possible by using the generally-employed hot alkaline electrolytes. An E. M. F. of 2 to 3 volts was maintained between electrodes 13 cm. (5⅛ ins.) apart, and good deposits continued to form.

The electrolyte is said to be suitable for the refining of tin, electroplating of tin, and electro-detinning of tin-plate scrap. The addition of ammonium salts, such as ammonium chloride, and organic substances, such as carbohydrates or gums, etc., is desirable for the production of brilliant deposits. (Metallurgie, 9, 492 (1912); Journal Society Chemical Industry, 31, 440 (1912).)

3. Steiner found that tin deposited from sodium sulphostannate electrolytes (See Sect. IV, 11) "could be still improved by adding a colloid to the electrolyte, for example, gelatine, as is used in the Betts' process for electrolytically refining lead."

4. E. F. Kern and A. P. Frapwell conducted experiments on the effect of certain organic addition-agents on the character of electrolytically deposited tin from solutions of sodium-stannous chloride, stannous fluoride, and sodium-stannous fluoride. (Results have been previously published.) These salts were selected on account of their solubility, and because their solutions are highly ionized and are excellent conductors.

(a) In Sodium-Stannous Chloride Electrolyte.—The solution was prepared to contain about 80 gms.

of tin and 50 gms. of sodium, as chlorides, per liter, by dissolving a calculated amount of sodium chloride in water, then adding a calculated amount of stannous chloride crystals. The electrolysis was conducted at ordinary temperature, using cast-tin anodes and tin-foil cathodes, with current-density of 10 amperes per square foot (0.9 amp. per sq. dm.). The distance between electrodes was about 1¼ in. (3 cm.), and potential about 0.1 volt. The deposit formed as a mass of bright needle crystals, which soon short-circuited the electrodes.

The effect of three addition-agents; gelatine, gum-arabic, and tannin was investigated, the electrolysis being conducted at the same temperature and current-density as above.

The presence of gum-arabic, in the proportion of 1 gm. per 800 to 1,200 cc. of solution, caused the deposit to form as small, bright, adherent crystals, which did not short-circuit the electrodes. The electrolysis was conducted for periods of 1 to 3 hours. The gum-arabic was added as an aqueous solution. It did not cause a precipitate to form when it was added to the electrolyte.

The addition of a solution of gelatine, and of tannin, caused a white collodial precipitate to form when added to the electrolyte. The deposit formed from electrolytes, to which the gelatine, and the tannin, were added in the proportion of 1 gm. per 500 to 1,500 cc. of electrolyte, were a mass of small bright needle crystals which could be rubbed off with a stirring rod. These two addition-agents caused the tin to be deposited as very small needles, whereas the deposits formed in the solutions which contained no addition were long dendritic needles.

(b) In Stannous Fluoride Electrolyte.—The solution was prepared by dissolving a weighed amount of stannous chloride in a small volume of water and adding a few cc. of hydrochloric acid to clear the turbidity. The tin was then precipitated by the addition of a concentrated solution of sodium carbonate, which gave a precipitate of stannous hydroxide. This was washed free of alkali by decantation, and finally filtered. It was dissolved in moist condition in a measured quantity of 40 per cent hydrofluoric acid, to give a solution containing a very slight excess of acid. This concentrated solution was diluted, so as to contain about 80 gms. of tin per liter.

The electrolysis was conducted at ordinary temperature using wax beakers for the cells, and cast-tin anodes and tin-foil cathodes. The current was passed at 10 amperes per square foot, with the electrodes about 1½ ins. (3.8 cm.) apart, and E. M. F. of 0.15 to 0.16 volt. The electrolysis was carried on for periods up to 8½ hours.

The deposits formed, with no addition-agent present, as a mass of loosely adherent sparkling dendritic needles, which soon caused short-circuiting. The anodes were evenly corroded, and remained very bright throughout the electrolysis.

The addition-agents tried were solutions of tannin, gelatine, gum-arabic, glycerine, resorcine, saccharine, grape-sugar, and glucose. The deposits were not much altered by any of the addition-agents except tannin, gum-arabic, resorcine and glucose. Tannin proved to be the most effective, and resorcine and glucose less effective than either the tannin or gum-arabic. The additions were made in small amounts of the aqueous solutions at a time, the first addition being in the proportion of 1 gm. per 2,000 cc. of electrolyte, then 1 gm. per 1,500 cc. of electrolyte, and so on by a 500 cc. decrease in the proportion of the electrolyte, until finally 1 gm. of the addition-agent per 100 cc. of the electrolyte had been added.

In the case when tannin was used, 1 gm. per 1,500 cc. of electrolyte caused the deposit to form finely crystalline and adherent. The best deposits formed when tannin was present.

The presence of gum-arabic in the proportion of 1 gm. per 1,500 cc. electrolyte caused a marked improvement in the deposition. Large proportions did not prove beneficial. In no case was a dense, smooth deposit formed.

With resorcine and glucose, not much improvement resulted until they had been added in the proportion of 1 gm. per 100 cc. of electrolyte, and even then the crystalline deposition was not restrained.

(c) In Sodium-Stannous Flouride Electrolyte.—This electrolyte was prepared in the same manner as the stannous fluoride electrolyte, with the addition of sodium fluoride. The solution contained 80 gms. of tin and 50 gms. sodium in the form of fluorides.

The electrolysis was conducted at room temperature (20 to 23° C.) in the same manner as the stannous fluoride electrolyte, but in this instance operating at current-density of 15 amperes per square foot (1.4 amp. per sq. dm.) The electrodes were placed 1¼ ins. (3 cm. apart, and the E. M. F. averaged 0.18 volt. The deposits formed as bright dendritic needles, which soon short-circuited the electrodes.

The same addition-agents were used as for the stannous fluoride electrolytes, they being added at regular intervals in small amounts at a time, until an apparent change in the characteristic appearance was noticed.

Tannin in the proportion of 1 gm. per 2,000 cc. of electrolyte caused the deposition of a smooth, very crystalline, firmly adherent coating. The run was continued for periods of 6½ hours. The anodes corroded evenly and remained bright. The potential between electrodes varied from 0.24 to 0.26 volt. Current-density of 15 amperes per square foot (1.4 amp. per sq. dm.)

Gelatine in the proportion of 1 gm. per 1,000 cc. electrolyte caused the deposit to form as adherent small crystals, with a few small dendrites on the edges of the cathode. It is not so satisfactory an addition-agent as tannin.

METHODS OF ANALYSIS USED IN THE LABORATORIES OF THE ARMOUR INSTITUTE OF TECHNOLOGY.

CEREAL ANALYSIS.

ESTIMATION OF NITROGEN.

The nitrogen in cereals is determined by securing it in the form of some ammonium compound then, after making the solution alkaline, the ammonia is volatilized and collected in acid of known strength. The procedure is as follows:

The substance is to be ground until it will pass a circular aperture 1 M. M. in diameter, or finer. Weigh out from .5 gram to 2 grams of the sample, depending on the probable percentage of nitrogen, transfer this to the flask and add .7 gram of metallic mercury, 25 c.c. of concentrated sulphuric acid free from nitrogen and 10 grams potassium sulphate. We find it convenient in transferring to the flask to have the neck of the flask dry, then using an aluminum spoon, which has been weighed with the sample and weighing bottle, transfer the requisite amount to the flask by tilting the flask and spoon simultaneously. This avoids the trouble arising from material adhering to the neck of the flask.

The flask and contents are then placed over a small flame of the Bunsen burner, in the hood, and heated slowly and carefully until all the material has passed into solution. The heat is then increased and continued until the acid solution is water white. About .5 gram of powdered potassium permanganate is then added, in small portions, the flask and contents are allowed to cool, 200 c.c. of water free from nitrogen is then added. Add 25 c.c. of potassium sulphide solution, shake well and allow to settle, then add 50 c.c. of NaOH solution, pouring the latter in carefully down the side of the flask so that it will remain in a layer under the acid solution, then add about a gram of finely granulated zinc, connect with the condenser, shake thoroughly and distill into the standard acid. The receiving flask should contain from 15 to 35 c.c. of accurately measured acid and should be diluted until the stem of the connecting bulb dips beneath the surface of the acid. Lacmoid is to be used as indicator. All of the ammonia will be found in the first 150 c.c. of the distillate, and when this amount has passed over, disconnect the bulb from the condenser, wash it out with distilled water, then titrate the excess of acid with n/10 ammonia. Calculate the percentage of nitrogen.

The factor employed to convert nitrogen to protein varies for the different cereals, being as follows: For wheat, 5.70; for oats, 6.31; for corn, 6.39; for barley, 5.82.

We have had trouble at times with portions of the alkaline liquor from the distilling flask being mechanically carried over. We have found only one safety distilling bulb tube which is satisfactory to prevent this. The tube we use is known as the Hopkins Modification of the Kjeldah distilling connecting bulb.

Trouble from the distillate being sucked back into the condenser is obviated by using a connecting bulb of ample capacity to contain all the distillate. This tube is drawn out to a point where it dips beneath the acid in the receiving flask.

Duplicates should agree to 1/10 c.c. HCl.

The reagent solutions are prepared as follows:

N/10 HCl.

From the percentage of actual HCl in the concentrated acid calculate the number of cubic centimeters needed per liter to make N/10 acid. When acid approximating the required strength has been prepared, determine its absolute strength as follows: To any convenient quantity of the acid, add silver nitrate solution in slight excess and 2 c.c. pure nitric acid, specific gravity 1.2. Heat to boiling point, with constant stirring, and keep at this temperature for some minutes without allowing violent ebullition, until the precipitate assumes the granular form. Allow to cool somewhat, then filter through asbestos in a weighted Gooch crucible. Wash the precipitate by decantation, with 200 c.c. of very hot water, to which has been added 8 c.c. of nitric acid and 2 c.c. of 1 per cent. silver nitrate solution. The washing by decantation is performed by adding the hot mixture in small quantities at a time, beating up the precipitate thoroughly each time with a thin glass rod after each addition. The pump is kept in action all the time, but the cover is only removed when solution is to be added. After the above washing of the precipitate, it is transferred to the crucible by using about one hundred centimeters of distilled water. The final washing is made with 20 c.c. of 98 per cent. alcohol. Dry at 120° to 130° until weight is constant.

N/10 Ammonia.

Make this solution such that 1.0 c.c. is equivalent to 1.0 c.c. of the N/10 hydrochloric acid solution.

Potassium Sulphide Solution—Dissolve 40 grams of the solid in one liter of distilled water.

Sodium Hydroxide Solution—Dissolve 500 grams of the solid in one thousand cubic centimeters of distilled water.

Determination of Moisture and Fat.—A glass inner tube of the Knorr extraction apparatus is provided with an asbestos mat, the tube is dried, weighed and about two grams of the cereal placed in the tube. The tube with contents is then dried at 105° C. for eight hours, cooled in a desiccator and reweighed, the final weighing being made in a counterpoised telescopic tube, as the dry cereals are hygroscopic. The loss in weight is moisture. The sample and tube which have been used for the determination of moisture are now placed in the Knorr extraction apparatus, which is connected with a Hopkins reflux condenser above and with a flask containing 150 c.c. of carbon disulphide below. The flask is placed on an electric lamp heater and the extraction is continued for four hours. At the end of this time the tube and contents are taken from the extractor, dried in the oven, cooled in the desiccator and weighed as described under moisture. The second loss in weight is fat.

Determination of Ash.—A weighed quantity of the food, preferably about two grams, is placed in a weighed and numbered porcelain crucible and heated in the muffle of a small gas, or better, an electric muffle furnace, until the ash is white or light gray. The heating must proceed slowly until all the carbon has been burned, then increased to about 1100°C. to complete the incineration.

Determination of Crude Fiber.—Extract 2 grams of the substance with carbon disulphide or use the residue from the determination of fat. To this residue, in a 500 c.c. flask, add 200 c.c. of 1.25 per cent sulphuric acid; connect the flask with an inverted condenser, the tube of which passes only a short distance through the rubber stopper into the flask. Boil at once and continue the boiling for 30 minutes. A blast of air conducted through the flask will aid in preventing foaming of the liquid. Filter on asbestos in a Gooch crucible; wash with boiling water until the washings are no longer acid; rinse the substance back into the same flask with 200 c.c. of 1.25 per cent sodium hydroxide solution, boil at once and continue the boiling thirty minutes, filter as before, wash until washings are neutral, dry at 105° in an oven, cool in the desiccator and weigh. Then incinerate completely. The loss in weight is crude fiber. Some materials filter very slowly; these are separated and washed in a centrifuge tube instead of being filtered.

The solution of sulphuric acid and of sodium hydroxide is to be made up of the specified strength, determined accurately by titration and not merely by specific gravity.

DETERMINATION OF CARBOHYDRATES.

(A) By Gravimetric Method (Estimated as Dextrose)—(1) *Reducing Sugars:*

Stir 3 grams of the sample in a glass container with 50 c.c. of water for an hour. Centrifuge and decant supernatant liquor, through hardened filter paper, into a 250 c.c. flask. The residue in the container is stirred up with 50 c.c. of water again centrifuged and liquid decanted. This is repeated three times. The volume of filtrate is then made up to 250 c.c. and is ready for use.

Determine reducing sugar by Allihn's method as follows: Place 30 c.c. of Allihn's copper sulphate solution, 30 c.c. of Allihn's alkaline tartrate solution, and 60 c.c. of water in a beaker and heat to boiling. To this mixture add 25 c.c. of the filtrate, prepared above, and which must contain not more than one per cent of dextrose, and *boil* for two minutes. Filter immediately without diluting. Be sure the filtrate is perfectly clear. Wash with boiling distilled water until the washings are no longer alkaline. Filter immediately through a weighed Gooch crucible, prepared with a thick asbestos mat. Wash with hot water until the washings are no longer alkaline, then wash with 10 c.c. alcohol. Follow with a wash of 10 c.c. of ether. Dry the crucible and contents for thirty minutes in a water oven, then cool in a desiccator and weigh. The weight of cuprous oxide multiplied by 0.8883 gives the weight of copper. From the weight of copper the quantity of dextrose is found by consulting Allihn's table (Ps. 50 & 51, Bulletin 107 revised.)

(2) *Estimation of Sucrose.*—Measure 50 c.c. of the sugar solution previously obtained into a 100 c.c. measuring flask, add 5 c.c. of concentrated hydrochloric acid, and place the flask in a water bath, the temperature of which is 70°. The contents of the flask should reach a temperature of 67 to 70° in two or three minutes, when the temperature should be maintained within these limits for exactly five minutes, keeping the temperature as near 69° as possible. The flask is then cooled rapidly and the solution after neutralizing with sodium carbonate, made up to 100 c.c. Determine reducing sugar in this solution by Allihn's method as given previously. Deduct the percentage of reducing sugar obtained at first and the remainder will be the reducing sugar derived from the sucrose; multiply this number by 0.95 to obtain the percentage of sucrose in the sample.

Estimation of Starch.—Transfer the insoluble residue obtained under (a) to a 500 c.c. flask and heat for 3 hours with 200 c.c. of water and 20 c.c. of hydrochloric acid (Sp. gr. 1.125), using a reflux condenser. Cool and neutralize with Na_2CO_3. Complete the volume to 250 c.c., filter and determine dextrose in an aliquot part of the filtrate by Allihn's method as given previously. The weight of dextrose obtained multiplied by 0.9 will give the weight of starch.

Preparation of Reagents.—(a) Copper sulphate solution. Dissolve 34.639 grams of $CuSO_4.5H_2O$ in distilled water and make up to 500 c.c.

(b) Alkaline tartrate solution. Dissolve 175 grams of Rochelle salts and 125 grams of potassium hydroxide in distilled water and dilute to 500 c.c.

CEMENT PRODUCTION IN UNITED STATES IN 1912.

According to an advance statement by Ernest F. Burchard, of the United States Geological Survey, the total quantity of Portland, natural, and puzzolan cements produced in the United States in 1912 was 83,351,191 barrels, valued at $67,461,513, compared with 79,547,958 barrels, valued at $66,705,136, in 1911. This represents an increase in quantity of 3,803,233 barrels, or 4.78 per cent, and in value of $756,377, or 1.13 per cent.

The distribution of the total production among the three main classes of cement in 1912 is as follows: Portland, 82,438,096 barrels, valued at $67,016,928; natural, 821,231 barrels, valued at $367,222; puzzolan, 91,864 barrels, valued at $77,363.

The total production of Portland cement in the United States in 1912, as reported to the United States Geological Survey, was 82,438,096 barrels, valued at $67,016,928, compared with 78,528,637 barrels, valued at $66,248,817, in 1911. The output for 1912 represents an increase in quantity of 3,909,459 barrels, or nearly 4.98 per cent, and in value of $768,111, or 1.13 per cent.

The shipments of Portland cement from the mills in the United States in 1912 are, according to reports received by the Survey, 85,012,556 barrels, valued at $69,109,800, compared with 75,547,829 barrels, valued at $63,762,638, shipped in 1911. The shipments therefore represent an increase in quantity of 9,464,727 barrels, or 12.52 per cent, and in value of $5,347,162, or 8.38 per cent. The average price per barrel in 1912, according to these figures, was a trifle less than 81.3 cents, compared with 84.4 cents in 1911. This represents the value of cement in bulk at the mills, including labor and cost of packing, but not the value of the sacks or barrels. The average price per barrel for the country is about 13.9 cents higher than the average price received for Portland cement in the Lehigh district, where it was sold at the cheapest rate, and is near the average price received in the Iowa-Missouri district, but it falls 54.5 cents below the average price received on the Pacific coast, where Portland cement brought the highest figure during the year.

Reports were received from nearly all the mills in the United States that shipped any Portland cement in 1912, giving stocks of finished cement on hand December 31, 1912. For the very few mills which did not report this information an estimate, believed to be very close, has been made. The apparent stock on hand at the end of 1912 amounted to 7,811,329 barrels, compared with 10,385,789 barrels on hand at the close of 1911, according to reports and revised estimates, thus indicating a reduction in stock of more than 2,500,000 barrels during 1912.

The imports and exports of cement are reported to the Survey by the Bureau of Foreign and Domestic Commerce. The statements include all hydraulic cements, also the weights of sacks or barrels. Portland cement probably makes up at least 95 per cent of the total in each year.

The imports of hydraulic cement in 1912 were approximately 68,503 barrels, valued at $93,558, or about $1.37 a barrel, compared with 164,670 barrels, valued at $242,722, or $1.47 a barrel, in 1911. This decrease in the quantity of cement imported was to be expected in view of the large excess domestic stocks that were marketed at low prices during the year.

The United States has a comparatively small export trade in cement. In 1912 the quantity exported was only 4,215,532 barrels, most of which was Portland cement, valued at $6,160,341, or approximately $1.46 a barrel, compared with 3,135,409 barrels, valued at $4,632,215, or about $1.477 a barrel, in 1911. The quantity exported in 1912 was slightly more than 5 per cent of the total production of hydraulic cements in 1912. The exports in 1910, 1911, and 1912 have shown increases of 135, 27, and 26 per cent, respectively, over those of the preceding year.

"FIRE SALE" OF GEOLOGIC FOLIOS.

As a result of the recent fire in the Geological Survey Building, the director has announced a "fire sale" of geologic folios. The entire basement, in which the folios were stored, was filled with dense smoke and many of the folios were burned, others scorched, and all more or less damaged by water. With the approval of Secretary Lane, the director announces that he will sell the entire remaining stock of some 150,000 folios, four-fifths of which are probably as near perfect as goods usually offered in a smoke or fire sale, at the nominal price of 5 cents each. The regular retail price of the standard folios is 25 cents, but a few unusually large folios have sold for 50 cents, and the regular price of the "field edition" of the later folios, a more convenient form for use in the field, is 50 cents. All these are now to be had at 5 cents each, but no wholesale rate applies to this fire sale. This would seem to be an excellent opportunity for students, engineers, and the public generally to order geologic folios to complete their files or to become acquainted with this Government publication, the 188 numbers of which fully describe the geology of some 175,000 square miles of the United States. The stock includes probably 50,000 to 100,000 copies on which the real damage is practically negligible. Application should be made to the Director, U. S. Geological Survey, Washington, D. C., and remittance made by money order or in coin. Lists will be sent on application.

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HARRY McCORMACK, Editor.

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NOTES AND COMMENTS.

The Wisconsin Label Decision.

The view that manufacturers of goods entering into interstate commerce *need pay no attention whatever to State laws* provided their products comply with the Federal Food Law, seems not to be accepted by all of the lawyers and officials who are interested in the recent United States Supreme Court decision handed down by Mr. Justice Day in the "Karo" Corn Syrup case, which set the Federal Law above the Wisconsin statute. On this subject James Foust, Dairy and Food Commissioner of Pennsylvania, says:

"Considerable conflict of opinion among those interested in the matter for food legislation as to the scope of the opinion of Justice Day, of the Supreme Court of the United States, in a decision recently handed down in the cases of McDermott vs. State of Wisconsin and Grady vs. State of Wisconsin. I asked the chief counsel of the Dairy and Food Bureau, A. H. Woodward, for an opinion as to the scope of these decisions, and as to their effect, if any, upon existing laws and pending legislation. The following is a resume of Mr. Woodward's opinion:

"The decision in the Wisconsin cases does not at all affect existing laws or pending legislation of Pennsylvania, as framed. The Supreme Court in the Wisconsin cases decides that a statute of Wisconsin, which requires a certain prescribed label, *and no other*, to appear upon packages of food imported into and sold in that State is in conflict with the National law because such statute plainly requires the destruction of the label under which the article was imported into the State, and thus destroys one of the means by which the United States Government, through its agencies, determines whether or not the article in question was, when imported, in conformity with the United States statute. The decision does not overrule, or attempt to overrule, previous decisions of the same court recognizing the right of a state, in the exercise of its police powers, to make laws and regulations controlling the sale of food commodities to the people of such State."—*American Perfumer.*

Utilization of Waste Raisin Seeds.

A Government bulletin entitled, "The Utilization of Waste Raisin Seeds," has recently been issued by the Bureau of Plant Industry. It is based on an investigation which proved that the seeds removed from raisins yield technically useful products that fully justify the expense involved in separating them.

In the raisin-seeding industry, which in recent years has grown to such proportions in California, vast quantities of seed accumulate annually. From 30,000 to 40,000 tons of raisins are seeded every year, and it is estimated that there should be in the neighborhood of 3,000 to 4,000 tons of the seed available annually. The utilization of this waste has received some attention by the producers in recent years, but thus far with little success. It appears that a brandy has been made by fermenting the sugary matter that adheres to the seeds, and that a high-proof alcohol has been distilled after the fermentation. It is also reported that some fixed oil has been obtained from the seeds.

The investigation described in the bulletin showed that four important products can be obtained from the waste seeds, namely, sirup, fixed oil, tannin extract, and meal. If the entire annual output of 3,000 to 4,000 tons of seed were used there would be obtained 550 to 740 tons of sirup, 340 to 460 tons of fixed oil, 330 to 445 tons of tannin extract, and 1,600 to 2,200 tons of meal.

Commercially the manufacture of sirup could be accomplished with comparative ease. Owing to the solubility of the sugars in water the process of preparation resolves itself into simple extraction and concentration. A clear transparent sirup with the characteristic flavor of the raisin can be produced from the sticky seeds. Its uses are many and should justify its production.

After washing off the sugary matter and drying and screening the seeds, they need only be ground for the production of the fixed oil. Two methods of extrac-

tion are feasible—by pressure and by solvents. The clear amber-colored oil is useful in paint and soap manufacture and possibly in other industries.

After the preparation of the sirup and the extraction of the oil from the seeds, the extraction of tannin is recommended. As the tannin is soluble in water it can be extracted in a practical way by boiling the meal in large digestion vats, the solution being transferred to vacuum pans for concentration to a moist extract. If a dry extract is preferred it can be obtained by simply allowing the moist extract to dry in the air.

The final residue—the meal—possesses useful qualities. While possibly it is not equal to some of the standard press cakes and meals for stock feeding, yet on account of its high protein content its usefulness as part, at least, of a stock-feeding ration can hardly be denied.

The properties of the four raisin-seed products and the commercial uses for which they are suitable are treated at considerable length in the bulletin.

Sixth Semi-Annual Meeting of the American Institute of Chemical Engineers.

The sixth semi-annual meeting of the American Institute of Chemical Engineers will be held at Boston, Mass., June 25-28. The headquarters will be at the Copley-Plaza Hotel. The program of the meeting is as follows:

Wednesday, June 25, 1913, 9:30 a. m.—Meeting at Engineers' Club, Arlington Street entrance.

Business session.

Reading of papers: "Effect of Climate on Plant Location," Wm. M. Booth; "The Power Plant," Mr. Barker, of Arthur D. Little, Inc.; "Relation of the Manufacturer to the Patent System," Dr. Wm. M. Grosvenor.

12:30 p. m.—Luncheon at Engineers' Club.

1:30 p. m.—Excursion to Watertown to visit the works of the Hood Rubber Co., manufacturers of rubber shoes, automobile tires, etc. (Not open to members connected with competing firms.)

Alternate excursion: U. S. Arsenal at Watertown and Laboratory and Experimental Paper Mill of Arthur D. Little, Inc.

6:30 p. m.—Informal dinner at Engineers' Club, $1.25.

8:00 p. m.—Presidential address, Dr. T. B. Wagner.

"General Efficiency in Dyehouses and Bleach Works," Dr. Louis J. Matos.

Thursday, June 26, 1913, 8:55 a. m.—Take train at Boston & Maine station for Lawrence, Mass. Two parties to visit one of the following plants:

(a) Pacific Mills (Cotton Goods and Prints).

(b) E. Frank Lewis' Wool Scouring establishment.

1:00 p. m.—Luncheon.

2:15 p. m.—Russell Paper Co. (Wood pulp by soda and sulphite processes, and manufacture of book and print paper.)

5:35 p. m.—Return by train to Boston.

7:00 p. m.—Informal dinner at Engineers' Club, $1.25.

8:00 p. m.—Evening session at Engineers' Club.

Reading of papers:

"Depreciation and Obsolescence," Richard K. Meade.

"Some Peculiar Functions of the Retained Expert," Dr. Wm. M. Grosvenor.

"Legal Control of Dangers to Health in Factories," Dr. Chas. F. McKenna.

Friday, June 27, 1913.—All-day excursion on special ocean going tug boat, as follows:

8:45 a. m.—Embark at Lewis Wharf on Atlantic Avenue, Boston, for the works of the New England Gas & Coke Co. at Everett, Mass. After inspection of this plant, re-embark for trip down the harbor and to Marblehead, Mass.

1:00 p. m.—Dinner at the Eastern Yacht Club, Marblehead. Return by the boat to Boston, stopping at the new Power Plant of the Boston Elevated Railroad, if time permits. Cost of excursion, including dinner at Marblehead, $5.00.

7:00 p. m.—Supper at Engineers' Club, $1.00.

8:00 p. m.—Evening session at Engineers' Club.

Reading of papers:

"Import Duties on Chemicals and Their Influence on Chemical Industry." By Dr. F. W. Frerichs.

"The Drying of Linseed Oil and Red Lead, with Special Reference to Painting Steel." By Dr. J. C. Olsen and A. H. Callaghan.

Final business session.

Saturday, June 28, 1913.—Excursion to Providence, R. I.

8:30 a. m.—Take train at South Terminal, New York, New Haven & Hartford Railroad. Due in Providence 9:05 a. m.

9:30 a. m.—Two parties to visit one of the following plants:

(a) Gorham Mfg. Co. (Silversmiths and Goldsmiths, Plated Ware, Bronzes, etc.)

(b) United States Finishing Co. (Large Cotton Finishing Plant. Bleaching, Dyeing, Printing.)

1:57 p. m.—Limited train for New York. (Special tickets and extra fare.)

2:03 p. m.—Afternoon express, due in New York at 6:30 p. m.

Both plants close at noon on Saturday.

BOOK REVIEWS.

Chemical Theory and Calculations.—By Forsyth James Wilson. D. Van Nostrand Co. New York. $1.

This book of 138 pages deals with the elementary calculations which are considered in General Chemistry. It gives in detail the methods employed in determining some of the physical purposes, such as: Specific gravity, vapor density, osmotic pressure and molecular weight. It deals quite fully with the theory involved in many of these determinations

and gives the mathematics necessary for making the desired calculations.

The book also discusses the methods employed in calculating formula from percentage composition as well as many problems arising in quantitative analysis and in thermo-chemistry.

The book is one which should be of considerable value in the hands of the student.

The Chemistry of the Rubber Industry.—By Harold E. Potts. D. Van Nostrand Co. New York. $2.00.

This most recent contribution of the Chemistry of the Rubber Industry begins with a chapter on the Colloidal State, which is of considerable importance in the study of the chemistry of rubber. It deals quite fully with the raw rubber, its collection, treatment, constitution, and analysis. Chapters are also given on the mixing of the rubbers and their vulvanization.

Vulcanized rubber is considered from the standpoint of its nature; the lines of chemical work involved in a study of vulcanized rubber and the methods methods employed in the analysis of vulcanized rubber.

The methods of analysis throughout are the ones most commonly employed by the chemists in the rubber industry and a rather full discussion of them is given.

Explosives.—By Dr. H. Brunswig. Translated by Charles E. Munroe and Alton L. Kibler. John Wiley & Sons. New York. $3.

This book deals very thoroughly with the physical chemistry involved in explosive reactions as well as the Explosive Industry in general. It is written primarily from the physical chemical standpoint and the desire of the author is to correlate the known behavior of the explosives with the physical chemistry of their constitution.

A very complete discussion is given of the uses of particular explosives.

The book is one of the latest and also one of the best publications we have covering the subject of explosives.

The American Fertilizer Hand Book for 1913. Ware Bros. Co. Philadelphia, Pa. $1.

This book, which is the most valuable publication we have covering the Fertilizer Industry in this country, has recently been received.

Some of the chapters in this issue which have been noted with particular interest and those which are given on The Fixation of Atmospheric Nitrogen; The Cyonamid Industry and the Menhaden Industry. The customary review of fertilizer prices for the year is given. Some valuable chapters on fertilizers for particular purposes are included.

This handbook is one of considerable value to all fertilizer manufacturers and others interested in the Fertilizer Industry.

Report of Proceedings, Ninth Annual Meeting. American Wood Preservers' Association.

The papers and discussion in this report which are of particular interest to the chemist are those on Preliminary Treatment of Timber to Insure a More Even and Satisfactory Impregnation with Creosote; Some Experimental Treatments with Reference to the Effect of Initial Air Pressure on Penetration of Creosote; On Treating with Petroleum Oil; On the Production and Supply of Coal Tar Crosote; The Analysis and Testing of Coal Tar Creosote; The Comparison of Creosote and Zinc Chloride Treatments, and the The Standard Specifications for Treatment.

New Publications on the West Virginia Geological Survey. New Edition.

(1) Coal, Oil, Gas, Limestone and Iron Ore Map issued under date of April 1st, 1913. This new edition is the joint publication of the State Geological Survey and the State Semi-Centennial Commission. It contains a thorough revision of the Coal, Oil, and Gas Developments, several anticlinals being added, and others corrected from later observations. The valuable iron ore deposits of the State are also indicated on this map, and all the special features of previous editions corrected and brought up to date, showing the approximate areas of the several coal series, operating mines and their postoffice addresses, as well as the oil and gas pools. Scale 8 miles to the inch. Price, enclosed in strong envelope and delivered by mail, 50 cents each, but in combination with other publications see general circular of the survey.

(2) Volume V (A), The Living and Fossil Flora of West Virginia, issued under date of June 1st, 1913, pages 491 +XIII. Part I, The Living Flora. By Dr. C. F. Millspaugh, a complete revision of the "West Virginia Flora," published in 1896, with many additions and new species brought up to date. Invaluable for students and teachers of Botany, Part II., the Fossil Flora. By Dr David White, giving a complete list of the fossil plants associated with each of the great coal beds, thus constituting a splendid guide to correlation. Price, including delivery charges, $1.50, but in combination, see general circular of the Survey.

RECENT PATENTS.

The following patents relating to industrial and engineering chemistry are reported by C. L. Parker, solicitor of chemical patents, McGill Building, Washington, D. C.

1,057,416. Process of Concentrating *Sulfite Waste Liquor.* Carleton Ellis, Montclair, N. J. Patented April 1, 1913.

1,057,422. Process of Making *Gold Pigment.* J. W. Hasburg, Chicago, Ill. Patented April 1, 1913.

1,057,423. Metal Alloy. Elwood Haynes, Kokomo, Ind. Patented April 1, 1913.

1,057,437. Manufacture of *Glycoheptonic Acid*. Arthur Liebrecht, Frankfort-on-the-Main, and Georg Rosenfeld, Breslau, Germany. Patented April 1, 1913.

1,057,564. Process and Apparatus for the Manufacture of *Steel*. Norman E. Maccallum, Phoenixville, Pa. Patented April 1, 1913.

1,057,667. Art of Treating *Asphalt*. James A. W. Pine and William B. Ruggles, New York, N. Y. Patented April 1, 1913.

1,057,680. Production of *Isoprene*. Karl Stephan, Charlottenburg, Germany. Patented April 1, 1913.

1,057,876. Process of Manufacturing *Nitrate of Lime* and *Dicalcium Phosphate* in a Single Operation. Samuel Peacock, Chicago, Ill. Patented April 1, 1913.

1,057,882. Process of Fusing and *Purifying Metals*. Walter S. Rockey and Hilliary Eldridge, New York, N. Y. Patented April 1, 1913.

1,057,886. Mode of Manufacturing a New Form of Synthetic *Indigo*. Albrecht Schmidt and Adolph Steindorff, Rochst-on-the-Main, Germany. The process consists in subjecting indol derivatives which are closely related to indigo and capable of directly yielding indigo to indigo-producing conditions in presence of a phenol. Patented April 1, 1913.

1,057,936. Treatment of *Copper Ores* Bearing Precious Metals. John C. Clancy, New York, N. Y. Patented April 1, 1913.

1,058,034. Method of Treating *Ores* and the Like. Niels C. Christensen, Jr., Salt Lake City, Utah. Patented April 8, 1913.

1,058,037. Process of Simultaneously Producing *Phosphate* and *Nitrate of Ammonia*. Emil Collett, Christiana, Norway. Patented April 8, 1913.

1,058,056. *Caoutchouc* Substances and Process of Making Same. Carl Harries, Kiel, Germany. Patented April 8, 1913.

1,058,145. Process of Manufacturing Solid *Fertilizer*. Frederick W. Braun, Los Angeles, Cal. Patented April 8, 1913.

Applications from Chemists, Engineers and Superintendents solicited for present and prospective vacancies. The Engineering Agency, Inc. (Est. 20 years), Monadnock Block, Chicago, Ill.

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MODERN BITUMINOUS ROADS AND PAVEMENTS.

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Perhaps no other subject today has such a genuine interest in the minds of the public as that of good roads. All over the United States as well as other nations, the people are awakening to the fact that good roads are essential to the rapid growth and development of the country. The ease and comfort of travel on highways are only acquired by proper improvement of the roadways.

The national government has a department devoted wholly to the advancement and aid in road building. Nearly every state in the Union has a highway department which looks after the building and maintaining of its roads. Every city has a department which is devoted to the improvement and maintenance of its streets and pavements. Millions of dollars are spent annually and yet the demand for more and better roads is rapidly increasing.

Up to the present time the United States Office of Public Roads has devoted its efforts to the aid of state and country work in demonstrative and advisory way but recently there was a bill introduced in Congress which provides for the building and maintaining of a system of national highways to be built and maintained by the national government. This system of roads would connect all the state capitols and cities of over 20,000 inhabitants. It would require 18,000 miles of roads at a cost of about $270,000,000.

Numerous societies have been organized for the advancement of the good road movement, among which are the Permanent International Road Congress, the American Highway Association, American Road Builders' Association, American Automobile Association, American Association for the Standardization of Paving Specifications, American Society for Municipal Improvements, and others.

The highway problems have for several years been attacked along scientific lines until road building has now become a science and an art. Specifications for the same classes of roads and pavements in different cities and states have varied so that an attempt has been made to standardize them and thus get better and more uniform results at a less expense. This work has been done largely by the American Association for the Standardization of Paving Specifications and the American Society for Municipal Improvement.

There are many types of construction of roads and pavements which might be of interest, but only those in which bituminous materials are used will be considered here.

The first bituminous pavement in this country was laid in Brooklyn in 1867. This pavement was a mixture of broken stone, gravel, ashes and tar. Soon after similar pavements were laid in Washington, D. C., and other towns with more or less success. In 1878 Trinidad asphalt was used in paving Delaware avenue, Buffalo, N. Y.; Newark, N. J.; New York City and Washington, D. C., soon followed in the use of asphalt, and from then until now its use has increased with surprising rapidity until there are now many million square yards of pavement in the United States laid with various kinds of asphalt, which have been produced to meet the great demand for it.

Bituminous pavements may be classified as follows: Sheet asphalt, asphalt block, asphaltic concrete, asphalt macadam, bituminous surfaces.

A sheet asphalt pavement is one consisting of a mixture of sand, dust and asphalt cement in varying proportions, spread on a firm foundation and rolled to an even surface. Usually the pavement is laid in two courses; the first, or binder, course consisting of a mixture of broken stone, with sometimes a little sand and asphalt cement. The thickness of the binder course varies from 1 in. to 1½ ins. The surface or top course, as described above, varies from 1½ to 2 ins. in thickness.

The foundation for all pavements should be firm and even. The surface and under-drainage should be ample to take care of all surplus water and thus insure the pavement against its damaging effects, which are principally the weakening of the foundation and the disintegration of the bituminous mixture from the emulsifying effect on the asphalt cement. This latter effect is much more noticeable with some asphalts, such as Trinidad, than others. For sheet asphalt nothing but a good concrete foundation should be used. Any sinking or giving of the foundation will cause defects in the surface which are difficult to repair.

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Every material entering into a paving mixture should be tested before its use. The sand, stone and dust comprising the mineral aggregate are tested for grading which consists in separating into different sizes by means of screens. The grading of the binder aggregate is not so important as that of the topping. The following are the limits given by the American Society for Municipal Improvements:

Passing 10 mesh	10-35%
Passing 2 mesh	10-35%
Passing 1 mesh	20-60%
Passing 1¼ mesh	15-55%

The quality and grading of the sand used in a top mixture is most important because it constitutes approximately 78 per cent of the mix. The following standard gradings are given by Richardson:

	Heavy traffic.		Light traffic.	
Passing 200 mesh	0.0		0.0	
Passing 100 mesh	17.0	34%	10.0	20.0%
Passing 80 mesh	17.0		10.0	
Passing 50 mesh	30.0		30.0	
		43%		45.0%
Passing 40 mesh	13.0		15.	
Passing 30 mesh	10.0		15	
Passing 20 mesh	8.0	23%	10	35.0%
Passing 10 mesh	5.0		10	

In practical construction it is seldom that a sand or combination of sands can be obtained, at a reasonable cost, that will conform strictly to the above gradings, but it is well to keep as near these limits as possible.

Richardson gives the following analyses as standards for top mixtures:

	Heavy traffic.	Light traffic.
Bitumen	10.5%	10.0%
Passing 200 mesh	13.0%	10.0%
Passing 100 mesh	13.0%	9.0%
Passing 80 mesh	13.0%	9.0%
Passing 50 mesh	23.5%	26.0%
Passing 40 mesh	11.0%	12.0%
Passing 30 mesh	8.0%	10.0%
Passing 20 mesh	5.0%	8.0%
Passing 10 mesh	3.0%	6.0%

To give an idea of how nearly these standards may be followed typical analyses of mixes used by the writer are given in Table I:

TABLE I.

	Bitumen.	200.	100.	80.	50.	40.	30.	20.	10.	Total.
Guthrie, Okla.	10.6	9.8	11.1	9.6	30.9	9.6	9.0	7.0	3.0	100
Sapulpa, Okla.	10.2	11.2	15.6	7.5	28.5	10.0	12.0	3.0	2.0	100
St. Louis, Mo.	10.3	11.4	6.0	17.0	35.0	5.3	6.0	5.0	4.0	100
Titusville, Pa.	10.0	8.0	7.0	17.0	34.0	7.0	8.0	5.0	4.0	100
Montreal, Can.	10.0	9.0	9.3	11.5	30.2	10.6	10.2	7.2	2.0	100
Victoria, B. C.	10.5	6.7	12.7	7.4	23.2	16.9	7.4	7.5	7.7	100
Spokane, Wash.	11.0	10.0	18.0	10.0	19.0	7.0	10.0	8.0	7.0	100
Wheeling, W. Va.	9.0	5.0	2.0	2.0	15.0	14.0	24.0	10.0	19.0	100
Standard	10.0	10.0	9.0	9.0	26.0	12.0	10.0	8.0	6.0	100

With each of the above mixtures most excellent results have been obtained. Some of the pavements have now been down four years with no repairs. The mixture at Wheeling, W. Va., is hardly to be recommended, and just how well it will wear is a question as it has been down less than a year, but is now in excellent condition.

The amount of asphalt cement used in a pavement mixture depends on the kind and quality of, first, the asphalt cement; second, the sand, and third, the filler or dust. All other things being equal, the specific gravity of the materials is the basis upon which the percentage of the ingredients of the mixture is determined. In other words, the ingredients should be used according to a percentage by volume rather than by weight. Considering the same aggregate it will take less asphalt cement by weight to cover every particle with the same thickness of asphalt using one having a specific gravity of .980 than it will with one having a specific gravity of 1.07. If the same asphalt cement be used with two different aggregates having the same grading and a different specific gravity, then the one having the greater specific gravity will require the lesser percentage of asphalt by weight because the surface per unit weight is less. The purity of the asphalt cement also affects the amount to be used. If an asphalt cement has a purity, i. e., bitumen soluble in carbon disulphide, of 99.5 per cent it will require less than one having only 56.0 per cent bitumen.

These differences are shown clearly by Table II:

TABLE II.

Various grades of asphalt.	% purity of asphalt.	No. lbs. bitumen per ton.	Gravity of pure bitumen.	Cu. ft. per ton.	Sq. yds. 2″ top laid per ton.
1	99.5	1,990	.980	32.5	98
2	56.0	1,120	1.071	16.7	51
3	94.5	1,890	1.068	28.3	86
4	71.0	1,420	1.086	20.9	63
5	99.5	1,990	1.050	30.3	92
6	99.5	1,990	1.045	30.5	92

The quality and grading of the sand are very important factors in determining the amount of asphalt cement to be used in a mix. If a sand is hard and smooth grained it will not carry as much asphalt as if it were softer and more porous, without producing a "sloppy" mixture, i. e., one in which the asphalt will flush to the top of a load after a little jarring. The river and lake sands are usually smoother and more rounded than the bank sands, due to the scrubbing and grinding action of the water. The bank sands seem to have a more porous surface, probably formed by a deposit of hydrosilicate about the surface of the grains. As a rule the finer the grading of the aggregate the more asphalt it will require to produce a satisfactory mixture. In extreme cases these two factors may cause a variance of as much as 3 per cent in the asphalt used.

What has been said about gravity and grading of sand applies equally well to dust as it is used as a filler to decrease the voids in the sand and to increase the toughness of the mixture. The most common fillers are limestone dust and Portland cement, which have from 70 per cent to 85 per cent of material which will pass a 200-mesh screen. In the State of Washington and the Province of British Columbia

there are large deposits of very fine sand, 65 to 80 per cent of which will pass a 200-mesh screen. These sands have been used very successfully as a filler in sheet asphalt.

There are a number of different kinds of asphalt used in sheet asphalt work and much has been written concerning them, therefore no attempt will be made to give a description of the different crude materials, but rather the sources, characteristics and qualities of the different asphalt cements which is the form in which the asphalt is used in the mixtures.

An asphalt cement, A.C., is prepared by refining and fluxing with a residuum oil, a crude native asphalt or semi-asphaltic oil until the residue has a penetration between 45 and 100 when tested at 25° C. for 5 seconds with a No. 2 needle weighted with 100. grams.

Table III gives the analyses of different asphalt cements as prepared and used by the leading companies of the United States in 1912. Included in this table are the following asphalt cements: Pioneer, Bermudez, Trinidad, Texaco, California, Cuban and Aztec. Pioneer is Utah gilsonite, a crude native asphalt, fluxed with a specially prepared flux. Bermudez is a natural asphalt, from a lake in Venezuela, fluxed with a heavy residuum oil. Trinidad is also a native asphalt, from a lake deposit in the island of Trinidad, fluxed with a residuum oil. Texaco is an oil asphalt prepared by distilling a crude Texas oil until the residue has the proper consistency. California is another oil asphalt prepared the same as Texaco but from crude California oil. Aztec has just been introduced on the market within the last two years and its value as a paving cement is questionable yet as it has had no service tests. It is prepared from a crude Mexican oil of which there is an abundant supply.

No attempt will be made to give a description of the methods used in making the above tests as a complete and detailed description may be found in Bulletin No. 38 of the U. S. Office of Public Roads.

The principal uses of the specific gravity tests are its aid in identifying the asphalt and in determining the percentage to be used in a mixture as described above. It is sometimes used as a method of control in the preparation of bituminous materials. It does not, however, indicate the value of a paving cement, as has been the contention of some engineers.

The melting point of an A.C. is a very important consideration in determining its suitability for use in a paving mixture. It will be noted from the table, No. I, that the melting points are fairly uniform with the exception of Pioneer, which is considerably higher. Upon careful examination of numerous pavements laid with these various materials it was found that those with the lower melting points were much more affected by the summer heat, getting soft and marking badly under traffic, while during the cold winter weather they became very hard and slippery. The material with the higher melting point did not show these effects nearly so much. Of course the susceptibility to temperature changes as shown by the different penetrations bring out these characteristics more clearly. It is not advisable to have too high a melting point though, for this makes the material much harder to handle and requires a higher temperature of the mixture which, of course, adds to the cost.

TABLE III.

Material.	Pioneer[1] A. C.	Bermudez[2] A. C. No. 2.	Trinidad[3] A. C.	Texaco[4] A. C.	California[5] A. C.	Cuban[6] A. C.	Aztec[7] A. C.
Specific gravity	.9930	1.0760	1.2880	1.0083	1.0453	1.0933	1.0455
Melting point	77°C.	61°C.	62.5°C.	64°C.	59°C.	61°C.	67°C.
Flash point (C. T.)	195°C.		205°C.	232°C.		215°C.	265°C.
Ductility 0°C.	3 cm	0 cm	8 cm	3 cm	0 cm	4 cm	0 cm
Ductility 25°C.	6 cm	40 cm	36 cm	21 cm	100 cm	28 cm	65 cm
Penetration 0°C. 200 gr. 1 min.	47	12	12	25	13	23	18
Penetration 25°C. 100 gr. 5 sec.	78	50	50	55	70	68	54
Penetration 46°C. 50 gr. 5 sec.	206	280	285	200	320	242	290
Loss 170°C. 5 hrs.	1.2%	3.3%	2.3%	.25%	1.4%	.3%	0.0%
Penetration residue 25°C.	58	21	21	38	27	17	37
Soluble in CS_2	99.77	94.15%	64.94%	99.65%	99.58%	89.38%	99.60%
Organic matter insoluble	.12	1.80%	5.33%	.10%	.22%	1.78%	.25%
Ash	.22	4.05%	29.73%	.25%	.20%	8.94%	.15%
Soluble in CCl 4	99.60	94.25%	65.58%	99.70%	99.60%	89.11%	98.75%
Soluble in 2 88° Beaume naphtha	71.53	70.17%	16.13%	74.00%	76.65%	67.68%	68.86%
Fixed carbon	9.43	10.21%	5.87%	9.84%	11.66%	9.70%	15.54%

[1]Pioneer is Utah gilsonite fluxed with a special flux. [2]Bermudez is a solid native bitumen fluxed with a residuum oil. [3]Trinidad is a solid native bitumen fluxed with a residuum oil. [4]Texaco is an oil asphalt prepared from crude Texas oil. [5]California is an oil asphalt prepared from crude California oil. [6]Cuban is a solid native bitumen fluxed with a residuum oil. [7]Aztec is an oil asphalt prepared from crude Mexican oil.

The penetration test is one of the most valuable in deciding upon the proper quality of the asphalt to be used. This test is made at three different temperatures, as follows:

1. 0°C. No. 2 needle weighted with 200 grs. for 1 minute
2. 25°C. No. 2 needle weighted with 100 grs. for 5 seconds
3. 45°C. No. 2 needle weighted with 50 grs. for 5 seconds

The first test is used to determine the proper consistency at which the A.C. is to be used and is a means of control in its preparation. If any one refined asphalt be fluxed to a certain consistency then all the other chemical and physical properties will change proportionately so that the one test is all that is necessary to make after complete analysis has been made at that consistency. The three tests combined are used to determine the susceptibility to tempera-

ture changes, which has a great bearing upon the characteristics of the pavement. A pavement laid with an A.C. which has a high ratio between the penetration at 0° C. and 45° C. will become very soft and will mark badly during the hot summer months, and in the cold winter months it will become very hard and slippery as well as noisy, while one laid with an A.C. having a low ratio between the penetration at 0° C. and 45° C. will not get so soft and mark up so badly in the hot summer months, nor will it get so hard, slippery or noisy in the winter months. These characteristics are very marked in pavements laid with the different materials.

The ductility test is claimed by many chemists and engineers to be a measure of the cohesiveness and cementitiousness of the asphalt and it is further claimed that a high ductility at 25° C. is essential to a good paving cement. Materials having a high ductility have a high susceptibility to temperature changes and become very hard and brittle when cold. From the above table it will be noted that the materials having a high ductility at 25° C. have no ductility at 0° C., while the one having a low ductility at 25° C. has about half as much at 0° C. It is when the pavement is cold that it contracts and needs a ductile material, when it is hot it expands and does not need it.

The loss at 170° C. for 5 hrs. and the penetration of the residue at 25° C. is determined to get by a quick method some idea as to what will be the effect of time on the cement after it is in the pavement. One having a high loss would naturally be affected more than one with a low loss, all other things being equal. An exceptionally high loss accompanied with a low flash point would indicate that too light an oil had been used for fluxing.

The solubility in carbon disulphide gives the purity of the asphalt, which is the amount of bituminous binding material in it.

Eighty-eight degrees Beaume paraffin naphtha separates the bitumen into two classes, each composed of various hydrocarbons. Those hydrocarbons insoluble in the naphtha give body and consistency to the asphalt cement, and is probably a measure of the adhesiveness. In the materials of the above table there is very little difference in the percentage soluble in 88° Beaume paraffin naphtha.

When an asphalt has been overheated some of the hydrocarbons will be broken down into compounds containing a very large percentage of carbon known as carbenes. These compounds are insoluble in carbon tetrachloride but soluble in carbon disulphide, so that their presence is determined by the difference in the solubility in the two solvents. It may happen in good asphalts which have not been overheated that they will be slightly more soluble in carbon tetrachloride than in carbon bisulphide. A very small percentage of carbenes will render a material unfit for use in pavements. The presence of carbenes may also be detected by a microscopic examination

The fixed carbon is determined by an arbitrary method the same as is used in coal analysis, and gives some idea as to the proportion of the heavier hydrocarbons present. It is of most value in testing oil asphalts such as California and Mexican, for these often show a very high percentage of fixed carbon which indicates that the asphalt has been distilled too rapidly at a high temperature. Fifteen per cent should be the maximum allowable fixed carbon content.

Among the most important features of a successful bituminous pavement is the proper handling of materials both at the plant and on the street. There is no doubt but that a majority of the failures are due either to carelessness or ignorance in construction. After a proper mixture has been determined it is essential that it be kept uniform, and the temperature be kept within certain limits, usually 275° F. to 375° F., depending on the melting point of the A.C. and the distance to be hauled. The question is often raised as to why the maximum temperature is only 375° F. when the temperature used in refining is in some cases 600° F. It is found that when the bitumen is in a thin coat around the hot particles of sand and stone that it burned at a much lower temperature than when heated in bulk and only a small proportion exposed to the air, therefore the temperature of the mixture must be lower.

The uniformity of the ingredients in a mixture can only be obtained by the most careful supervisions. It is necessary to make tests of the grading of the mineral aggregate at least three or four times a day and tests for bitumen from representative "pot" samples should be made at least twice a day.

The laying on the street consists of spreading, raking and rolling. When a load reaches the street it is dumped from the wagon just far enough ahead of what has been laid so that the shovellers can spread it without having to carry any ahead. After spreading it should be well raked and "combed" until it is true to grade. The raking is very important and only experienced men should be employed. The rolling is usually done with two rollers, a five-ton and an eight-ton. The first or surface rolling is done with the smaller roller just as quickly as the material is cold enough so that it will not blister under the roller. A water spray is used on the wheels of the roller to prevent the mixture picking up or sticking to the wheels. If the surface rolling is delayed until the mixture gets too cold it will "honeycomb" and the proper compression will not be obtained. In some cases the surface will chill so that no amount of rolling can thoroughly compress it and the pavement will be porous and absorb water, which will be shown by the surface remaining damp for a long time after a rain. When this condition exists the water will freeze and the expansion will cause the pavement to

disintegrate. In one case a pavement constructed with California where this condition existed, a heavy rain followed by freezing and thawing weather caused the asphalt which became hard and brittle to break loose from the aggregate and was washed into the gutter. The surface rolling should be followed by a thin coat of Portland cement swept over the surface just ahead of the larger roller which is run very slowly, giving the surface a straight and double diagonal roll until it is smooth, even and free from roller marks and will show no indentation from the roller.

Sometimes the rolling will produce numerous surface cracks extending from ¼ in. to 1 in. in depth. This may be caused by movement of the binder stone, slipping or creeping of the top on smooth concrete when no binder course is used or a burnt or dry mixture, i. e., one without sufficient A.C. in it.

An asphalt block pavement is one composed of blocks about 2 in. by 4 in. by 8 in. made by compressing with about 240 tons pressure a mixture of ½ in. stone chips, sand, dust and A.C. An A.C. with a very low penetration, usually 15, is used in making these blocks, as well as a very low percentage of bitumen. The following is a typical analysis:

Bitumen	7.5%
Passing 200 mesh	13.0%
Passing 100 mesh	5.0%
Passing 80 mesh	3.5%
Passing 50 mesh	6.0%
Passing 40 mesh	5.0%
Passing 30 mesh	4.0%
Passing 20 mesh	6.0%
Passing 10 mesh	14.0%
Passing 8 mesh	7.0%
Passing ¼ mesh	22.0%
Passing ½ mesh	7.0%

The blocks are laid similar to brick on a concrete foundation with about 1 in. cushion of a 1-3 sand cement mix fairly dry.

Asphaltic concrete is a pavement composed of a mixture of crushed stone, sand, A.C. and in some cases dust. There are three distinct types of asphaltic concrete which will be designated as type A, B and C.

Type A is what is known as the Topeka mix. This name was given it because it is the mix described in the specifications of Topeka, Kan., upon which the Warren Bros. Co. of Boston tried to get an injunction against the city on the grounds of infringement of their patent No. 665,725. The court ruled that this was not an infringement.

The specifications for this mix are as follows:

Bitumen	7-11%
Mineral aggregate—	
Passing 200 mesh	5-11%
Passing 40 mesh	18-32%
Passing 10 mesh	25-55%
Passing 4 mesh	8-22%
Passing 2 mesh	less than 10%

Some pavements laid under this specification are given a flush or squeegee coat of asphalt, followed by a thin coating of clean ½ in. crushed rock screenings or coarse torpedo sand. The purpose of the flush coat and screenings is to fill the surface voids and seal it, making it impervious to water. The screenings are worked into the flush coat by traffic until it finally has an appearance similar to sheet asphalt.

The crushed rock used should be trap, "hard heads," granite, hard limestone or any good durable stone. It is better to have the stone free from dust as it is usually distributed very ununiformly which makes it difficult to get a uniform grading of the aggregate, besides this the dust is apt to form a crust about the particles of stone if it becomes wet and when dried it will not come off and when the asphalt is added it does not penetrate to the stone and thus the mixture will be apt to have loose stones which are liable to cause raveling, i. e., picking out of the stone under traffic.

The A.C. used in this class of work is very similar to that used in sheet asphalt, in fact some companies use the same material.

In this class of construction the low ductile asphalts such as "Pioneer" are particularly well adapted especially where a flush coat is used as it does not get brittle and chip out under traffic in cold weather as the high ductile materials do. In order to overcome this ravelling some companies use a much higher per cent of asphalt in the mix, e. g., in New York City last year one company used as high as 10.6 per cent of Mexican asphalt. A sample from this work showed the following analysis:

Bitumen	10.6%
Passing 200 mesh	7.0%
Passing 80 mesh	15.0%
Passing 40 mesh	19.0%
Passing 20 mesh	20.4%
Passing 10 mesh	10.0%
Passing ¼ mesh	13.0%
Passing ½ mesh	5.0%

This pavement may be laid on concrete, macadam, old brick or stone as a foundation. If it is laid on macadam great care must be taken to see that there are no soft or spongy places in it, but if the macadam is good, equal if not better results may be obtained.

What has been said regarding the construction of sheet asphalt pavements applies equally well to asphaltic concrete and as this subject was discussed in some detail, it will not be repeated here.

This class of pavement has become very popular in the last two years, many thousand yards have been laid with excellent results. It is particularly well adapted to heavy automobile traffic with medium horse drawn traffic. In New York City last year over 100 miles were laid. A great deal of it having a very heavy horse drawn traffic with heavy auto traffic and a recent inspection of these pavements found them in good condition except where there had been faulty construction.

Asphaltic concrete Type B consists of a mixture of crushed stone varying in size from that passing in a 1-inch ring to that retained on an 8-mesh screen and asphalt, no sand or dust being used. This type requires much less asphalt in the mixture but must have a flush coat of about ¾ gal. per square yard with a

coat of screening as described under Type A.

What has been said of the quality of stone under Type A applies equally well to Type B.

The A.C. used is much softer as shown by the following analyses:

	Pioneer.	Bermudez.
Specific gravity	.9866	1.0242
Melting point	137°F.	117°F.
Flash point (C. F.)	430°F.	360°F.
Penetration at 0°C.	69	19
Penetration at 25°C.	81	110
Penetration at 45°C.	221	too soft
Loss at 170°C. 5 hrs.	.33%	2.92%
Penetration of residue 25°C.	68	65
Solubility in C. S_2	99.86%	97.42%
Solubility in CCl_4	99.80%	97.88%
Solubility in 88° Be. naphtha	73.25%	74.51%
Fixed carbon	9.20%	9.83%

Coal tars and water gas tars have also been used for this type of pavement, particularly in the eastern states but they are so susceptible to temperature changes and pavements laid with them get so hard and slippery that they have not been very popular. A great deal of experimental work has been done with tar asphalt mixtures. About 12-15 per cent of asphalt is the maximum that can be used safely with a tar. If an excess is used it will get "cheesey" and have no binding power. When a small percentage of asphalt is used the tars are improved because the asphalt makes them less susceptible to temperature changes and more stable. The following are typical analyses of these materials:

	Coal tar.	Water gas tar.
Specific gravity	1.258	1.158
Float test at 50°C.	2 min. 30 sec.	23 sec.
Soluble in CS_2	70.4%	98.9%
Organic matter insoluble	29.5%	1.1%
Ash	.1%	.05%
Distillation—		
Oils to 110°C.	.2%	.03%
110-170	.6%	.05%
170-270	10.2%	10.00%
270-315	7.5%	19.10%
Residue	81.4%	69.40%

Type C is a patented pavement, similar to Types A and B. It is composed of stone such as is used in Type B and sand. This requires a little more A.C. than Type B but not so much as Type A. The following are the grading limits given in the patent:

Impalpable powder	1-3%
Impalpable powder to ¼"	10-30%
¼" and larger	50-80%

Below is a typical analysis of a pavement of this class:

Bitumen	6.0%
Passing 200 mesh	1.7%
Passing 80 mesh	2.5%
Passing 40 mesh	8.8%
Passing 10 mesh	35.6%
Passing 8 mesh	16.8%
Passing 4 mesh	5.2%
Passing 2 mesh	18.2%
Passing 1 mesh	5.2%

It is claimed by the patentees that the grading used gives a minimum of voids producing a maximum density and inherent stability in the pavement which cannot be obtained by either Type A or B. This, however, has been disproved by the excellent results obtained with the other classes of pavements. Their claim that a minimum in percentage of voids can only be obtained by such a graded aggregate has also been disproved by the writer in some tests made recently in which less than 16 per cent of voids were obtained in a mixture of one sized crusher run of stone; i. e., passing a 1-inch ring and retained on a ¾-inch ring and sand.

Asphalt macadam is a pavement constructed by what is known as the penetration method, and is as follows: Upon a crushed stone foundation, similar to a water-bound macadam is spread about 3 in. of clean stone, which will pass a 2-in. ring and be retained on a ¾-in. ring, and rolled to an even grade when it will be about two inches thick. Over this is spread either by pouring cans or other distributors about 1½ gals. of bituminous binder to the square yard. A thin coating of clean ¾-in. crushed stone is spread over the surface and then thoroughly rolled. The excess of stone is swept off and a second pouring of about ½ gal. to the square yard is applied followed by a thin coating of clean ½-in. stone chips, when the pavement is again well rolled.

This is perhaps the most uncertain of any of the types of bituminous pavements for there are so many important details which are essential that are often neglected. Only first class stone, uniform in size should be used in this class of construction. The pouring should be done with the greatest care and only after thorough rolling and when the stone is clean and dry. It is almost impossible to keep from getting the bituminous material in streaks when the pouring can is used. The Eldus, which is a hand drawn distributor, has given more uniform results. Many excellent roads have been built by this method but it requires a great deal of skill and attention to get good results. One great advantage is its low first cost which is a great item on country roads where traffic is light.

The bituminous binders used in asphalt macadam are much softer than in sheet asphalt as will be seen from the following typical analysis:

	Pioneer.	Bermudez.	Texaco.
Specific gravity	.969	1.0427	.9862
Melting point	116°F.	109°F.	liquid
Flash point (CF)			
Ductility 23°F.	4 cm	34.2 cm	
Ductility 0°C.	2 cm	2.0 cm	
Penetration at 0°C.	95	37	too soft
Penetration at 25°C.	183	132	too soft
Penetration at 45°C.	too soft	too soft	too soft
Loss at 170° 5 hrs.	2.0%	4.64%	9.0%
Penetration of residue at 25°C	138	33	139
Solubility in C S_2	99.95%	96.04%	99.5%
Solubility in CCl_4	99.96%	95.96%	99.4%
Solubility in naphtha 88° Be.	76.25%	77.30%	82.2%
Fixed carbon	7.74%	10.84%	8.53%
Paraffin scale	3.14%	.84%	.22%

All of the above tests were discussed under sheet asphalt except paraffin scale. There has been a great deal of discussion as to the value of this test and at present its value is very questionable owing to the fact that no standard method is in use by which uniform and consistent results can be obtained. A large sample divided and sent to half dozen different prominent chemists brought as many different results, varying from 1 to 5 per cent. In each case the same

method was supposed to have been used. By slightly varying the details of distillation results varying from 1½ to 4.5 per cent were obtained by the writer, using the same apparatus and same sample.

Bituminous surfaces are used on water-bound macadam and gravel roads. These surfaces are formed by applying a heavy residuum oil to the clean dry surface of the road and then covering with a thin coating of clean stone chips or coarse sand. These surfaces are well suited to medium automobile traffic where there is not an excess of horse drawn traffic.

The first cost of a treatment as described above is very low but it has to be repeated from twice a year to every two years depending largely on the bituminous material used and the traffic conditions.

Just recently a special material for this class of work has been on the market and has been used very successfully on water-bound macadam, brick and sheet asphalt pavements. It is similar to those used in penetration work but is exceptionally adhesive.

A water-bound macadam treated with ½ gal. per square yard two years ago is in excellent shape. An old brick pavement similarly treated has the appearance of a bituminous pavement. A sheet asphalt pavement which was badly cracked and had started to disintegrate was repaired by a surface treatment and is in good shape. These instances are mentioned because so many attempts along this line have failed. The following is an analysis of this material:

Specific gravity	97.42
Melting point	117° F.
Penetration at 0° C.	62
Penetration at 25° C.	175
Penetration at 45° C.	Too soft
Loss at 170° C., 5 hrs.	2.44%
Penetration of residue at 25° C.	105
Solubility in CS_2	99.83%
Solubility in CCl_4	99.86%
Solubility in 88° Be. Naphtha	79.03%
Fixed carbon	6.79%

Many attempts have been made to get a bituminous surface to adhere to a concrete pavement but have been only partially successful. Light tars will adhere for a time but as soon as they get cold they become brittle and chip off under traffic. Asphalts have been used but traffic seems to abrase the surface of the concrete forming a fine dust which allows the bituminous surface to peel off.

In conclusion it might be said that while the intelligent use of bituminous materials in road construction is well understood by a large number of chemists and engineers there is yet room for much research and experimental work which will no doubt be done in the near future as the popularity of the bituminous pavement is so rapidly increasing.

The silk industry in Italy employs 190,000 operatives, operates 62,000 basins, 1,500,000 spindles and 19,000 looms; 40 per cent located in Lombardy, 40 per cent in Piedmont and Venetia and the remainder in central and southern Italy.

PRELIMINARY REPORT FOR THE COMMITTEE ON COAL ANALYSIS OF THE AMERICAN SOCIETY FOR TESTING MATERIALS AND THE AMERICAN CHEMICAL SOCIETY.*

BY W. A. NOYES.

INTRODUCTION.

Sometime ago committees were appointed by the American Society for Testing Materials and the American Chemical Society for the purpose of revising the standard methods of coal analysis. During the fall of 1911 the two committees were organized as a joint committee consisting of the following members: W. A. Noyes, chairman; Perry Barker, H. C. Dickinson, A. F. Fieldner, Frank Haas, W. F. Hillebrand, S. W. Parr, S. S. Voorhees, A. H. White.

At the Washington meeting of the American Chemical Society in December, 1911, this committee met and after a careful discussion of the problems to be considered appointed the following sub-committees:

1. Preparation of samples, including loss of moisture in sampling—Mr. Fieldner, chairman, Haas, Hillebrand, Voorhees, Parr and Barker.
2. Moisture—Dr. Hillebrand, chairman, Fieldner, Parr.
3. Deterioration—Prof. Parr, chairman, Fieldner, Haas, Dickinson.
4. Volatile Matter—Prof. Parr, chairman, Fieldner, Haas, Dickinson.
5. Fixed Carbon and Ash—Prof. Parr, chairman, Fieldner, Hillebrand.
6. Sulphur—Mr. Barker, chairman, Voorhees, Dickinson.
7. Phosphorus—Dr. Hillebrand.
8. Ultimate Analysis—Mr. Fieldner, chairman, Parr, White.
9. Calorimetric Determination—Mr. Dickinson, chairman, Haas, Barker.
10. Interpretation and Computation—Whole Committee.

These sub-committees have been actively at work and at the Milwaukee meeting in March it was decided to publish at the present time a preliminary report of the work of each sub-committee, which it is hoped will furnish the basis for discussion on the part of members of the committee and of others who are interested in the matter, to the end that it may be possible at the Rochester meeting in September to carry the discussion far enough to make it possible to present a final report in the near future. The reports of the sub-committees, which are given below, are in all cases the results of a considerable amount of correspondence and discussion, but it is to be clearly understood that these recommendations are not final and have not been endorsed by the committee as a whole, and indeed in several cases it has not been

* From the Journal of Industrial and Engineering Chemistry.

possible to carry the discussion far enough so that it can be said that the report represents fully the sentiment of the sub-committee. In other words, the chairmen are primarily responsible for these reports in their present form.

Every one interested in the subject of coal analysis is earnestly urged to read these reports and to send to the chairman any suggestions which he thinks may be of value to our committee. As an introduction to these reports, the following items, which are partly the result of the discussion at Milwaukee, may be mentioned:

It can not be emphasized too strongly that in coal we have an extremely complex mixture of organic compounds, many of which are easily changed by oxidation and otherwise by exposure to the air, and containing water in such condition that a part of it is usually lost with the greatest ease, while the material after complete drying is excessively hygroscopic, probably even more so than calcium chloride. These actual conditions give rise to variations in analysis very far beyond those which most analysts, who have not studied the matter carefully, realize. It has seemed necessary, therefore, to the committee to place rather liberal estimates on the allowable variations in the analysis, and in addition to this we wish to impress it upon every analyst that it is necessary for him to convince himself by personal experiment (1) *that the variations in his own method of procedure do not cause errors greater than the allowable amount, and* (2) *if possible, that the methods give results which will agree with those of other analysts.*

Sampling.—A committee of the Society for Testing Materials on coal specifications, of which Mr. J. A. Holmes, of the Bureau of Mines, Washington, is chairman, has charge of the questions relating to the sampling of coal under different conditions, in the mine, on cars, in bins, etc. By mutual agreement that committee considers all questions up to the point of furnishing to the laboratory a five-pound sample, which our committee think should be of one-eighth inch size and which, of course, must be submitted in a sealed can under conditions to prevent loss of moisture and deterioration. It was the consensus of opinion at Milwaukee that in the preparation of this five-pound sample at least fifty pounds of coal should be crushed to one-eighth inch size by a suitable mill. A mill which is suitable for this purpose is sold at a price of $7.50 by the Enterprise Manufacturing Company, Philadelphia. In sampling and analyzing it is necessary to emphasize again the fact that coal is an extremely changeable substance, that all operations should be carried out as rapidly as possible, and that the analysis should be made as soon as practicable after the sample reaches the laboratory.

Moisture.—It is probably impossible to secure an actually exact determination of the amount of moisture present in coals, especially in those of the bituminous or lignite type, partly because some compounds in the coal decompose readily with loss of water, and partly because of the rather rapid oxidation of such coals when heated in the air. The determination of moisture is, therefore, to be considered as empirical rather than theoretical, and we should strive at conditions that should give concordant results, the agreement of different analysts being of more importance than a determination of the actual amount of moisture in the coal, since the calorific value of the "pure coal" depends on the method of determining moisture in such a manner that it is unimportant whether some of the moisture is counted as moisture or as a part of the coal.

Volatile Matter.—The determination of the volatile matter is empirical even to a much greater extent than that of moisture, and here again the point that must be aimed at is to secure conditions which can be accurately reproduced by different analysts. The most important change which seems necessary from the procedure recommended by the committee of the American Chemical Society in 1899 is the application of a gentle heat at first to those lignites which undergo a large mechanical loss if the full heat is applied at once.

Ash.—Practically it is expected that for the present, at least, the ash which will be reported by coal analysts will be that which is found by careful burning of the coal at a temperature finally reaching about 700-750° C. Theoretically, however, the ash should include all substances in the coal other than moisture and organic compounds which are combustible. It seems desirable, therefore, to introduce as a basis for careful work, especially for the calculations of engineers, a "corrected ash" which would include iron pyrites, sulphur, calcium carbonate, calcium sulphate, ferrous sulphate and the water of hydration of clayey matters which is not expelled at 110°.

Calorimetric Determination.—As brought out by Mr. Fieldner, under conditions of actual practice, coals are always burned in such a manner that the water escapes as vapor. It is probably not possible at once and perhaps not soon to induce engineers to change their practice of basing their calculations on the calorific value of coals burned to liquid water, but we think that in all cases in the future the statement of calorific values should have appended to it either the words "liquid water" or "vapor of water at 20°."

In conclusion, I wish to express our thanks to many chemists not members of our committee who have coöperated with us and participated in our discussions, especially to H. C. Adams, Horace C. Porter, W. H. Blauvelt, J. D. Davis, William Brady, W. B. Wiley, L. A. Touzalin and A. C. Parsons.

Preparation of Laboratory Samples.

By A. C. Fieldner, Chairman.

AMOUNT AND FINENESS OF SAMPLE FOR TRANSMITTAL TO THE LABORATORY.

Assuming thorough mixture, accuracy in the reduction of gross samples to a convenient quantity for

transmittal to the laboratory, is largely dependent on crushing the extraneous impurities of slate, pyrite, etc., to such a degree of fineness before each process of mixing and dividing, that the inclusion of a few pieces more or less in the various divisions can not materially change the character of the final sample.

That there should be a nearly constant ratio between the largest particle of heaviest impurity and the weight of sample, in the various stages of reduction is essential, otherwise excessive errors are introduced at the particular point in the process where this ratio is exceeded. Hence the quantity of sample to send to the chemist will be governed by the relative proportion of free impurities and the practical limits of fineness to which these impurities can be crushed at the point of sampling.

Bailey[1] places the following limits beyond which samples should not be divided when crushed to different sizes:

Size of impurities.	Minimum weight of sample.
2-mesh	8300 grams (18.3 lbs.)
4-mesh	1100 grams (2.5 lbs.)
8-mesh	120 grams

His table is based on a ratio of 0.02 per cent between the weight of the largest pieces of slate and the minimum weight of sample. For the above limits of reduction in the case of samples containing 5 per cent ash as free impurities, Bailey computes the probable error in ash at 0.20 per cent and the maximum possible error occurring once in 10,000 times at 1.00 per cent ash.

Somermeier[2] gives the following table as a guide in selecting and reducing samples containing pieces of pyrite equivalent to cubes of different sizes:

Size in inches.	Weight of sample. Grams.	oz. or lbs.
1/64	1	1/28 ounce
1/32	8	2/7 ounce
1/16	64	2 2/7 ounces
1/8	510	1 1/8 pounds
3/16 (a)	1700	3¾ pounds
1/5 (a)	2090	4 3/5 pounds
¼	4090	9 pounds
⅜	13700	30 pounds
½	32700	72 pounds

(a) Interpolated by the writer. Size of openings in 4-mesh sieves vary from 3/16 inch to 1/5 inch, depending on thickness of the wire.

The above table is based on a ratio of 0.019 per cent between the weight of ash resulting from the largest particle of pyrite and the weight of sample.

This ratio according to Somermeier is sufficiently small to keep the error in ash less than 0.5 per cent, provided the sample is thoroughly mixed and properly reduced.

The results of a considerable number of sampling experiments made by the Bureau of Mines indicate that the quantities of sample given in the above table for various sizes of particles are none too large.

The sub-committee, therefore, recommends the following minimum weight of sample for transmittal to the laboratory:

Size of largest impurities.	Minimum weight of sample.
½ inch	75 pounds
⅜ inch	30 pounds
¼ inch	9 pounds
3/16 to 1/5 inch (a) (4-mesh)	5 pounds
⅛ inch	3 to 5 pounds

(a) The usual 4-mesh screen has openings of 3/16 inch to 1/5 inch in length.

SPECIAL MOISTURE SAMPLES.

Unless special crushing and sampling apparatus is available, much moisture is lost during the reduction of the gross sample to the smaller sizes given above. Therefore, when the moisture content is important, a special moisture sample should be accumulated by placing in a hermetically sealed receptacle small parts of the freshly taken increments of the gross sample.[3] These parts should be broken to about ½ in. size as accumulated. If possible, the mixing should be done in the closed receptacle, and an average sample of about 3 lbs. quickly transferred to a moisture-tight container for shipment to the laboratory.

Mine samples when reduced in the mine do not require a special moisture sample, owing to the usual high humidity of mine atmospheres.

CONTAINERS FOR SHIPMENT TO LABORATORY.

Samples in which the moisture content is important should always be shipped in moisture-tight containers. A galvanized iron or tin can with a screw top which is sealed with a rubber gasket and adhesive tape is best adapted to this purpose. Glass fruit jars sealed with rubber gaskets may be used, but require very careful packing to avoid breakage in transit.

Samples in which the moisture content is of no importance need no especial protection from loss of moisture.

PREPARATION OF LABORATORY SAMPLES.

The method of preparing a suitable sample for the various analytical determinations that are required in coal analysis must conform as nearly as practicable to the following requirements:

(1) A uniform distribution of coal and impurities must be maintained throughout the process of reducing to the final powdered sample. This should be insured by thorough mixing between each dividing or quartering process, and by having due regard to the ratio of size of largest impurities and weight of sample as given in the preceding tables.

(2) Changes in moisture during the procedure of sampling must be reduced to a minimum.

Coal, especially when in a pulverized condition, is exceedingly susceptible to change in moisture content. The general tendency is loss of moisture on dividing to finer sizes. This may amount to several per cent in coal that has not been previously air dried.

The equilibrium point of the moisture in pulverized coal varies with the temperature and humidity of the

[1] "Accuracy in Sampling Coal," by E. G. Bailey, this Journal, 1, 176 (1909).

[2] "Coal, Its Composition, Analysis, Utilization and Valuation," by E. E. Somermeier, page 67, McGraw-Hill Book Co. (1912).

[3] See page 29, Bull. 63, Bureau of Mines, "Sampling Coal Deliveries," by G. S. Pope (1913).

air. Coal that has reached equilibrium with respect to moisture in an atmosphere of low humidity will reabsorb moisture if placed in an atmosphere of higher humidity.[4]. Hence to reduce the loss of moisture to a minimum the sample received by the laboratory should be brought to an approximately air-dry condition, before it is pulverized and reduced to the final sample for analysis. Furthermore, the unavoidable exposure of the sample to the air of the sampling room both before and after the air-drying period must be limited to the shortest possible time. The use of an air-tight grinding apparatus such as the ball mill is essential for the final pulverization.

The result[5] of a considerable number of experiments comparing the ball mill and bucking board at the United States Fuel Testing Plant show that air-dried samples rubbed down on a bucking board may gain or lose moisture, depending on the extent of previous air-drying and the humidity conditions of the sampling room.

If the sample has not been air-dried, or if a ball mill is not available, a special moisture sample should be taken after the coal has been rapidly reduced to 10- or 20-mesh size. The main portion of the sample may then be pulverized and reduced by any suitable apparatus without regard to further moisture changes. The sample obtained by this method will be more susceptible to loss of moisture while weighing out portions for analysis, than air-dried samples. The moisture must, of course, be accurately determined in both samples to bring the calculations to the same wet or dry basis.

(3) Due regard must be given to the tendency of coal to absorb oxygen and deteriorate in heating value.

That appreciable quantities of oxygen are absorbed during prolonged air-drying at 35° C. is shown by the following experimental results obtained by H. C. Porter, of the Bureau of Mines:

"The coal in the above tests was used in the condition as received from the mine sampler, having been crushed by him so as to pass through a 2-mesh screen. The sample was mailed to the laboratory in a galvanized iron can, sealed moisture-tight.

"There are two sources of error in these tests, both of which tend to lessen the oxygen absorption: (1) the coal was in a confined space with no circulation of air, so that the moisture vapor arising from the coal was not displaced by air as readily as in the usual air-drying process; and (2) the normal oxygen content of the air was not maintained constantly, the supply of fresh oxygen being admitted only once in 24 hours.

"The results show, however, that the oxidation error during air-drying at 35° C. may amount in the case of a sub-bituminous coal to at least 0.4 per cent in 4 days and 0.7 per cent in 8 days. The calorific values determined on such an air-dried sample will be in error to a somewhat larger extent, owing to the neutralizing effect of oxygen on the hydrogen and carbon of the coal."

Mine samples of coal crushed to 4 mesh (3-16 inch to 1-5 inch) and spread out to a depth not exceeding 1 inch, in circulating air at 10° C. above room temperature will become approximately air-dry in the following periods of time:

Appalachian coals ..... 8 to 24 hours
Illinois and similar coals ..... 12 to 48 hours
Sub-bituminous coals and lignites ..... 48 to 72 hours

Lignites and some sub-bituminous coals continue to lose moisture over longer periods of time than given above; however, in view of Porter's experiments, the above maximum limits should not be exceeded.

OXYGEN* ABSORBED BY 100 GRAMS OF COARSELY CRUSHED COAL (AS RECEIVED) OF EXPOSURE TO AIR AT 35° C., REPLENISHING THE OXYGEN OF THE AIR INTERMITTENTLY AS ABSORBED.

	Fresh mine sample of bituminous coal from Pittsburgh bed. Air-drying loss (usual method)=2.5 per cent.		Fresh mine sample of sub-bituminous coal from Wyoming. Air-drying loss (usual method) =14.2 per cent.	
Days.	Cc. oxygen absorbed (0° C. and 760 mm.)	Percentages by weight of oxygen absorbed	Cc. oxygen absorbed (0° C. and 760 mm.)	Percentage by weight of oxygen absorbed
1	43	0.06	81	0.12
2	71	0.10	155	0.22
3	71	0.10	204	0.29
4	87	0.13	264	0.38
5	100	0.14	312	0.45
6	109	...	...	...
7	...	...	377	0.54
8	123	...	419	...
Correction (a)	6	—	64	—
8	117	0.17	483	0.70

(a) Based on analysis of air in container, before and after.

MOISTURE REMOVED DURING TEST.

Pittsburgh coal ..... 2.46 per cent
Wyoming coal ..... 5.27 per cent

*Quoted from private communication from H. C. Porter.

METHODS OF SAMPLING RECOMMENDED BY THE SUB-COMMITTEE.

The following alternate methods of preparing laboratory coal samples are recommended as conforming to the theoretical requirements set forth in the pre-

[4]For experimental data on moisture changes in coal samples, see Bull. 28, Bureau of Mines, "Experimental Work of the Chemical Laboratory," by N. W. Lord.

[5]"Experimental Work of the Chemical Laboratory," by N. W. Lord, Bull. 28, Bureau of Mines, and Bull. 323, U. S. Geological Survey.

*Quoted from private communication from H. C. Porter.

[6]For details of air-drying oven see Bull. 9, 4th series, Ohio Geological Survey, "Coal," by Bownocker, Lord and Somermeier (1908), page 312, or Technical Paper 8, Bureau of Mines. "Methods of Analyzing Coal and Coke," by F. M. Stanton and A. C. Fieldner (1912), page 4, or "Coal, Its Composition, Analysis, Utilization and Valuation," by E. E. Somermeier, page 71, McGraw-Hill Book Co. (1912).

[7]For details of riffle sampler see Bull. 9, 4th series, Ohio Geological Survey, page 313, or "Coal, Its Composition, Analysis, Utilization and Valuation," by E. E. Somermeier, page 73.

ceding paragraphs, and as being commercially practicable for technical coal analysis:

METHOD I.

Samples of coal received by the laboratory which exceed 5 lbs. in weight, or 4 mesh (length of openings in sleeve not to exceed 0.20 inch)in size should be rapidly crushed to 4 mesh, mixed and reduced to not less than 5 lbs. This portion is then transferred to a weighed sheet-metal pan, spread out to a depth of 1 inch and at once weighed. The pan is placed in a special drier[6] and the coal allowed to air-dry in circulating air at 10° C. to 15° C. above the sampling room temperature, until the rate of moisture loss is less than 0.1 per cent per hour, as shown by two weighings made at intervals of 2 to 4 hours. The time limits already given in this report should not be exceeded. In most cases bituminous coal and anthracite will be air-dry if left in the drier over night.

Immediately after the last weighing has been made, the entire sample should be rapidly pulverized to 10-mesh size, mixed and reduced to 500 grams with an enclosed riffle, sampler[7] whose sub-divisions are not more than ½ in. apart. This 500-gram portion is at once transferred to the porcelain jar (8.95 in diameter and 9.65 in. high) of an Abbé ball mill, sealed air-tight and pulverized to 60-mesh. Bituminous coals require about ½ hour and anthracites about 2 hours to pulverize to 60 mesh.

The jar should contain about one-third of its volume of 1-inch, well rounded flint pebbles, and should be rotated at about 60 revolutions per minute. The coal is removed from the porcelain jar by emptying the contents on a ½ in. screen, which is vigorously shaken a moment to detach the coal from the pebbles. The sample is then reduced to the final laboratory sample of approximately 60 grams by successively halving it with a small, enclosed riffle sampler. All of the final sample should then be put through the 60-mesh sieve, and at once transferred to a 4-ounce wide-mouthed bottle which is securely closed with a well fitting rubber stopper. Tc avoid moisture change the sieve should be covered while sifting. Usually a few particles of coarse material remain on the sieve. These must be rubbed down on a bucking board or mortar to 60-mesh, and thoroughly mixed with the sample. (If one could be certain that all of each sample would pass the 60-mesh sieve it would be preferable to omit sieving, since it has a tendency to segregate the particles of slate and pyrite and offers an opportunity for change in moisture content. On the other hand, if the sieving is omitted there is great danger of rather coarse particles of slate and pyrite being present in the final sample). The mixing and reducing of the sample after removal from the ball mill should be done rapidly to minimize loss or absorption of moisture. The total time elapsing from the opening of the ball mill jar to the stoppering of the laboratory sample bottle need not exceed two or three minutes.

The total loss in weight of samples while air-drying is reported as air-drying loss.

METHOD II.

Samples of coal if larger than 4-mesh (0.20 in.) should be rapidly reduced to 5 lbs. at 4- mesh or finer as in Method I.

This 5-lb. portion is quickly passed through a suitable crushing apparatus—rolls or enclosed coffee mill type of grinder, adjusted to crush to 10 or 20-mesh size. A 60-gram moisture sample should be taken, without sieving, immediately after the material has passed through the crushing apparatus. This sample should be taken with a spoon from various parts of the 10 or 20-mesh product, and should be placed directly in a rubber-stoppered bottle.

The main portion of the sample is further pulverized until all passes through a 20-mesh sieve. It is then thoroughly mixed and reduced on the riffle to about 120 grams, which is pulverized to 60-mesh by any suitable apparatus without regard to loss of moisture. After this sample has been passed through the 60-mesh sieve it is again mixed and divided on a small riffle to 60 grams. The final sample should be transferred to a 4-oz. rubber-stoppered bottle.

Coal containing visible superficial moisture should be spread out in weighed pans and allowed to air-dry as in Method I, or at room temperature, otherwise considerable loss of moisture will take place while crushing to 10-mesh size. The percentage of loss in weight is recorded and the analysis of the air-dried sample corrected to the "as received" basis.

Notes on Method I.—(1) This method of preparing coal samples was developed by Lord and Somermeier at the Fuel Testing Plant of the U. S. Geological Survey at St. Louis. It has been used for several years by the Bureau of Mines in connection with the analysis of mine samples of coal, where especial consideration must be given to loss of moisture during the sampling process. The Bureau of Mines uses a chipmunk jaw crusher for crushing the sample received at the laboratory to 4-mesh size, and a Sturtevant roll crusher for reducing the 4-mesh material to 10 or 20-mesh size. The rolls have one disadvantage, in that with some coals, flakes are formed which must be broken up by rubbing through a sieve before the sample can be reduced on the riffle. On the other hand, the rolls have a large capacity and are easily cleaned.

Coffee or bone mill types of grinders may be used for grinding to 10- or 20-mesh size. They should be entirely enclosed and provided with a covered hopper and receptacle of sufficient capacity to hold the entire 5-pound sample.

(2) A new porcelain jar ball mill and pebbles should always be tested for abrasion before use. This may be done by grinding 500 grams of sugar for a period of 2 hours, and then determining the ash in

[7] For details of riffle sampler see Bull. 9, 4th series, Ohio Geological Survey, page 313, or "Coal, Its Composition, Analysis, Utilization and Valuation," by E. E. Somermeier, page 73.

the sugar; or by keeping a record of the loss in weight of jar and pebbles and the weight of coal ground. No trouble has ever been experienced by the Bureau of Mines in the use of the ball mill.[8]

(3) A large number of duplicate sampling experiments by Method I, beginning with a 3- to 5-pound 4-mesh sample have been made by the Bureau of Mines on a wide range of coals. The variations in moisture usually range from 0 to 0.20 per cent and the variations in ash from 0 to 0.4 per cent.

A COMPARISON OF TOTAL MOISTURE IN DUPLICATE SAMPLES OF COAL.

Description of coal.	Sample No.	Total moisture. Sampled by Method I per cent.	Total moisture. Sampled by Method II per cent.	Difference.
Bituminous, Pittsburgh bed, dry...	10	1.99	1.74	—0.25
Bituminous, Pittsburgh bed, dry...	11	1.97	1.76	—0.21
Bituminous, Pittsburgh bed, dry...	12	1.97	1.74	—0.23
Bituminous, Pittsburgh bed, wet...	13	3.46	2.92	—0.54
Bituminous, Pittsburgh bed, wet...	14	3.62	2.74	—0.88
Bituminous, Pittsburgh bed, wet...	15	3.55	2.84	—0.71
Bituminous, Pittsburgh bed, dry...	16	2.80	2.58	—0.22
Bituminous, Pittsburgh bed, dry...	17	2.67	2.56	—0.11
Bituminous, Pittsburgh bed, dry...	18	2.81	2.57	—0.24
Sub-bituminous, Wyoming, dry....	19	15.99	15.56	—0.43
Sub-bituminous, Wyoming, dry....	20	16.21	15.61	—0.60
Sub-bituminous, Wyoming, dry....	21	15.89	15.62	—0.27

Notes on Method II.—(1) This method requires less special apparatus (such as air-drier, and ball mills) than Method I, and, therefore, can be more readily adapted to the apparatus at hand in the ordinary analytical laboratory. The sample can be prepared for analysis in a much shorter time than by Method I.

The moisture obtained by this method is usually somewhat lower than by Method I, as shown in the preceding table of experimental results obtained on duplicate samples analyzed by Methods I and II.

(2) The Bureau of Mines has used this method during a period of several years in the Fuel Inspection Laboratory at Washington. The samples as received, if larger than ¼ in., are first pulverized with a jaw crusher to about ⅛ in. and then by a roll crusher to 20 mesh. A planetary disk grinder is used for pulverizing to 60 mesh. This machine, on account of heating, can not be used for anthracite.

Duplicate samples almost invariably check within 0.4 per cent in ash.

(3) For crushing samples in the field S. W. Parr recommends a small portable mill which will reduce the samples to ⅛ in. size before quartering.

(4) S. W. Parr and W. A. Noyes recommend that all samples should be crushed to ⅛ in. size in the field and reduced to not less than five pounds before transmittal to the laboratory.

(5) The size to which the final laboratory sample should be pulverized is best indicated by showing the deviation in ash and sulphur that is caused by one particle more or less of cubes of pyrite equivalent to the openings in the various sizes of sieves.

Nominal size of sieve.	Length of opening mm.	Weight of pyrite cub equivalent to opening Gram	Weight of sulfur in this cube Gram	Weight of ash produced from this cube Gram
40 mesh.....	0.42	0.00037	0.00019	0.00024
60 mesh.....	0.34	0.00020	0.00011	0.00013
80 mesh.....	0.23	0.00006	0.00003	0.00004

An inspection of the above table shows that 40 mesh is obviously too coarse to insure satisfactory duplication, inasmuch as a deviation of only 10 particles of pyrites in the 1-gram sample would cause a difference of 0.19 per cent sulphur and 0.24 per cent ash. Even 60 mesh is scarcely fine enough for high-sulphur coals. In such cases 80 mesh would be preferable.

Silk mill electrification is to be carried out at Leek, England, where a preliminary plant enables the managers to plan extensions making it possible to produce current at not over 1.10 cents per unit.

The first button factory in Mexico has been started in Mexico City. Ecuadorian ivory nuts are used. The government has sent circulars throughout Mexico to see if button material may be found or the ivory-nut tree introduced.

The following are the specifications "52V6," March 15, 1913, of the U. S. Navy Department for ferric oxide varnish:

1. Ferric oxide varnish shall be of the best quality and manufacture and shall consist exclusively of hard varnish resins, pure spirits of turpentine, pure linseed oil, and lead or manganese driers, or both, and be free from all adulterants or other foreign materials.

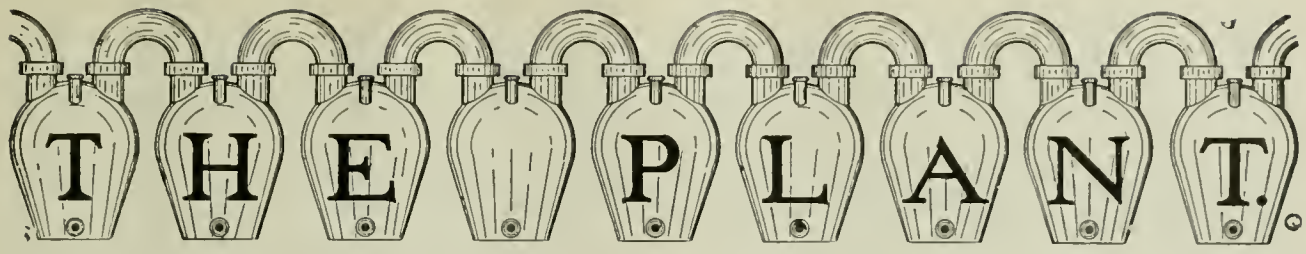
2. The varnish must not flash below 105° F. and when flowed on glass must set to touch in less than 2 hours and dry hard in less than 8 hours in a temperature of 70° F. The varnish shall contain not more than 55 per cent of volatile vehicle.

3. Each bidder must state in his proposal the name of the manufacturer, the grade or trade name, and the age of the varnish he will guarantee to deliver.

4. Deliveries shall be made as specified; if in 5-gal. cans, such cans shall be packed two cans to a case, cans and cases to be in strict accordance with the latest specifications for the same issued by the Navy Department.

5. Each can of varnish delivered and every case in which the cans are packed must be properly marked with the name of the material, the trade-mark, if any, the name of the manufacturer, quantity contained, the contract number, and the number of the requisition on which the material was purchased.

[8] For experimental data on abrasion in ball mills see paper on "Accuracy and Limitations of Coal Analysis," by A. C. Fieldner, The Journal of Industrial and Engineering Chemistry, 5, 281 (1913).



PHOSPHATIC FERTILIZERS.*

By PROF. W. PALMAER.

In order to meet the ever growing demand of agriculture for phosphate fertilizers, chiefly the following preparations are at present produced: Acid phosphate, basic slag, bone meal, bicalcic phosphate, which are here given in the order corresponding to the amount produced, acid phosphate being the phosphate fertilizer most largely produced, the annual output amounting to about 10,000,000 tons.

Bicalcic phosphate so far has been produced only in small quantities, the production in Germany and France, for instance, during 1910, amounting to about 5,000 tons for each country. To date this product has been obtained only as a by-product in the manufacture of glue, i. e., in the process when bone is soaked in diluted hydrochloric acid, whereby the main product in the manufacture, the glue substance, remains undissolved, while a solution of bone phosphate is obtained as a by-product. This is turned to account by precipitation with lime, by which means bicalcic phosphate is obtained.

On the other hand it is a long while ago since it was first proposed to obtain bicalcic phosphate as the chief product from every kind of raw phosphate in the same way, viz., by extracting the raw phosphate with hydrochloric acid and precipitating the solution thus obtained with lime. This method would have the advantage that one could make use of very poor and otherwise valueless raw phosphate, provided it does not contain too large a proportion of any useless, soluble compound, such as carbonate of lime. In the production of acid phosphate, on the other hand, one can not utilize raw phosphate with a lower percentage than about 50 per cent bone phosphate, since owing to the admixture of gypsum the percentage in the acid phosphate of available phosphoric acid is only about half that of the raw phosphate's percentage of phosphoric acid, and consequently consideration of freight charges for the prepared article excludes the use of a raw material in which the percentage is low.

However, it has been found that the price of hydrochloric acid has been too high for the adoption of this method. This in its turn is due to the fact that the production of hydrochloric acid according to the old methods entailed the sacrifice of sulphuric acid.

But the case is different if the acid is produced in such a way that a suitable salt, for instance perchlorate of sodium, is electrolyzed with a diaphragm, so that free acid is generated in the anode chamber, and a solution of caustic alkali in the cathode chamber. With an electrolyzing tension of 4½ volts and 80 per cent current efficiency it is easy to calculate that in order to produce the kilogram equivalent of acid 182 horsepower hours are required, whereby the alkali necessary for the precipitation of the bicalcic phosplate is obtained at the same time without additional cost in the cathode chamber. If we assume that one electric horsepower can be obtained for $10 a year—the usual price in many parts of Europe and presumably in many places in America—then the cost of the equivalent of one kilogram of acid amounts to about 24 cents, the alkali being obtained at the same time; while with the old method lime had to be purchased. There is no outlay for material beyond what is caused by spilling, etc., as the electrolyte regenerates, as will be seen from what follows.

If we assume that the price of one ton of chamber acid with 65 per cent H_2SO_4 is $5, we shall find that the cost of the kilogram-equivalent of H_2SO_4 (49 kg.) is about 38 cents.

This calculation consequently shows that provided the remaining outlay for the electrolytic process can be kept within reasonable limits, it should be assured of success, especially as it allows of the utilization of otherwise valueless raw phosphate or refuse.

This calculation was the basis of my investigations, the object of which was consequently to try to make the method economically feasible, chiefly by finding a suitable electrolyte, and by constructing a serviceable electrolyzer.

As in the process there is no consumption of chemicals, beyond loss by spilling, etc., the cost of the sulphuric acid used in producing acid phosphate is replaced by the cost of the electric power. The economic result of the method depends therefore in the first place on the price of the power.

Before entering upon detailed descriptions, a general survey of the method will be of advantage.

GENERAL FEATURES OF THE METHOD.

In an apparatus expressly constructed for the method, a solution of chlorate or perchlorate of sodium is electrolyzed. In the anode chamber an acid is thereby generated—chloric or perchloric acid—and in the cathode chamber a solution of caustic soda. The electrolysis is continued until a certain quantity of the dissolved salt has been separated into acid and alkali. The anode and cathode solutions are led off

* Paper presented at Eighth International Congress of Applied Chemistry.

into separate receivers. The acid anode solution is then allowed to work in a dissolving battery upon raw phosphate, in which process the phosphate is dissolved. Into the solution thus obtained the alkaline cathode solution is introduced, the whole being meanwhile kept vigorously stirred, until the liquid bears evidence of a slightly acid reaction; to obtain that result about half the cathode solution is required. In the process bicalcic phosphate is precipitated as a finely crystalline precipitation, which is drained off by filtration and washed. The filtrate, which contains one-third of the lime originally dissolved, but hardly any phosphoric acid, now has added to it the remainder of the cathode solution, which has previously been saturated with carbonic acid from fuel gas. The lime is precipitated as carbonate, which is allowed to settle. The solution remaining above it is then drawn off. The original electrolyte is regenerated by its means, and again enters the electrolyzing apparatus.

Of course, the hydrogen, obtained as a by-product at the cathode in the electrolysis of the salt solution, could be used for making ammonia or in any other way thus increasing the value of the products obtained.

THE NATURE OF THE ELECTROLYTE.

With reference to the electrolyte, the salt used should be of such a nature that its acid may yield, in conjunction with lime, an easily soluble salt and of a kind which is not subject to change during electrolysis.

As electrolytes, solutions of perchlorate of sodium or chlorate of sodium are suitable, or else mixtures of those salts, the presence in small quantities of other salts, for instance, chlorides, being of no account. Both these salts can now, since they are being produced by electrolysis, be had at reasonable prices. Nitrate of sodium cannot be used because it is too strongly reduced at the cathode to nitrate, ammonia, etc.

Perchlorate of sodium is an ideal electrolyte for the purpose in question. On electrolyzing its solution with a diaphragm, sodium hydrate is formed in the cathode chamber, and perchloric acid in the anode chamber, while hydrogen is developed at the cathode and ozonic oxygen at the anode. No noticeable reduction of the salt occurs at the cathode, nor any other change, and the solution of perchloric acid obtained is perfectly constant at such temperatures as occur in the electrolyzing (maximum, 50° C.). Furthermore, the salt is exceedingly easily soluble (deliquescent), and thus easy to wash away.

Chlorate of sodium is less constant in that the chloric acid solution formed in the anode chamber already begins to decompose at 40° C., free chlorine being developed. Moreover, it is considerably reduced at the cathode to chloride. But the principal change is that the development of oxygen at the anode almost ceases, because the chlorate there is oxidized to perchlorate. For this reason a start can very well be made with chlorate of sodium, since, though the drawbacks mentioned (the decomposing of the chloric acid and the reduction of chlorate) appear at first, they soon disappear, viz., when the chlorate has become perchlorate of sodium. Even if you begin with chlorate of sodium, the electrolyte consists after a while of pure perchlorate, which, as has been said, suffers no further change.

The loss of perchlorate of sodium by spilling and incomplete washing need not, according to our experience, be estimated higher than at about 1 per cent of the weight of the bicalcic phosphate developed.

Another way of carrying out the process is this: A solution of chloride of sodium is electrolyzed so that a solution of caustic soda and free chlorine is obtained. The chlorine is transformed in the usual way into hydrochloric acid, wherewith the raw phosphate is dissolved, whereupon a precipitate is formed with this caustic soda. The salt is then regenerated as before. Although common salt is cheaper than perchlorate of sodium or chlorate of sodium, the process, by several reasons (depreciation of anodes, loss of chlorine, etc.), is not so advantageous.

THE ELECTROLYSIS.

The electrolysis of the perchlorate of sodium solution must be carried out, as has been mentioned, in a diaphragm apparatus, and it is clear that the problem is to find a suitable anode and a suitable diaphragm. Both difficulties have been solved in a perfectly satisfactory manner, but for the present I cannot enter into details.

The voltage has been found to amount on the average to 4.5 volts per cell, including loss in connections. It varies somewhat, depending on the age of the diaphragms, the efficiency of the electrical contacts and the temperature of the solutions, which may vary at different times of the year; but, as stated, the average voltage is 4.5. The polarization amounts to 2.97 volts.

In a diaphragm process, where the new substances formed at the cathode and the anode remain in the solution (in this case alkali or perchloric acid), the current efficiency continually diminishes, of course, in proportion as the newly formed substances begin to take part in the current circuit. We generally produce solutions with 1 gram-equivalent of acid or alkali per liter, and have then a current efficiency of 82 per cent and a ballast of undecomposed salt in both acid and alkali solutions.

THE RAW MATERIAL AND ITS UTILIZATION.

Of course, the high percentage raw phosphates used to make acid phosphate can be employed for the process, but it is not for such, but rather for low percentage raw phosphates, at present worthless or of inferior value, that the process is primarily designed. Here I need only mention in illustration low percentage apatites and apatite waste, waste from magnetic separation of phosphoric iron ore and certain low percentage phosphorites.

As the process consists in dissolving the bone phosphate occurring in raw phosphate, and then precipitating bicalcic phosphate from the solution, the product

obtained will always be of the same nature, irrespective of the percentage of the raw phosphate. We have employed raw products whose percentage of bone phosphate varied between 20 and 88 per cent.

Furthermore, the raw phosphate need not be finely pulverized, provided that the bone phosphate is not embedded in insoluble minerals and that other soluble substances, such as certain silicates, do not occur in too great a quantity. We have worked with material of as coarse crushing as 5 cm.

Assuming that the solution of bone phosphate is effected according to the formula $Ca_3P_2O_8 + 6HClO_4 = 3Ca(ClO_4)_2 + 2H_3PO_4$, then per liter of normal acid 23.7 grams of phosphoric acid should be dissolved. It can be foreseen, however, that the reaction in contrast, for instance, to the reaction $CaCo_3 + 2HClO_4 = Ca(ClO_4)_2 + H_2O + CO_2$ will not proceed quantitatively, since phosphoric acid is a much stronger acid than carbon dioxide. We have also found that we must reckon with a somewhat lower figure, say 20 gr. P_2O_5 or 43.6 gr. $Ca_3P_2O_8$ per liter of normal acid. This figure holds good provided that no other bodies soluble in acids occur in the raw phosphate.

Of such, in the first place, we must take into consideration calcium carbonate, for, as we know, it readily and completely dissolves in acids. As the equivalent weight for phosphoric acid (P_2O_5) is 23.7, and for carbon dioxide (CO_2) 22, we can consequently state that 1 per cent of CO_3 in the raw phosphate causes approximately the same consumption of acid (or of energy) as 1 per cent of P_2O_5, without giving any product of any value to speak of (the amount of carbonate of lime obtained as a by-product will, of course, be correspondingly greater). A raw phosphate which contains 20 per cent of P_2O_5 (as $Ca_3P_2O_8$) and 2 per cent of CO_2 (as $CaCO_3$) consequently requires about 10 per cent more energy than a raw phosphate with the same proportion of phosphoric acid but free from carbonate of lime.

Iron oxides (iron ores), on the other hand, are only dissolved very slightly. We found that after twenty-four hours' shaking at the usual temperature with normal acid there was dissolved of magnetite a quantity corresponding to 0.24 gr. Fe_2O_3 per liter from hematite, a quantity corresponding to 0.20 gr. of Fe_2O_3 per liter, which amounts are of no practical importance.

Most silicates are, as we know, insoluble in diluted acids However, silicates may occur, for instance, together with apatite, which are so easily soluble that they dissolve to a noticeable degree if the acid is in contact with them for any length of time after most of the phophate is dissolved. Attention must be paid to this in the course of the lixiviation, and the work regulated accordingly.

As regards the utilization of the bone phosphate in the raw material, we can as a rule count upon extracting 98 per cent of it, sometimes more, sometimes a little less, viz., when easily soluble silicate is present.

PRECIPITATION OF THE BICALCIC PHOSPHATE AND CALCIUM CARBONATE.

To precipitate the bicalcic phosphate we made use, as before stated, of the solution of caustic soda obtained by electrolysis and saturated afterwards by carbonic acid, which is introduced into the phosphate solution by means of a sprayer.

The employment of the soda solution as a precipitant, instead of milk of lime, has a considerable advantage. For the fact is that as soon as the solution has become alkaline at any point, bone phosphate is precipitated there instead of bicalcic phosphate. This once precipitated bone phosphate is only slowly converted into bicalcic phosphate, even if the average acidity of the liquid is such that only bicalcic phosphate ought to occur. At least a portion of the bone phosphate thus formed remains therefore in the precipitated bicalcic phosphate. The bone phosphate thus precipitated is very finely distributed, it is true, and is even soluble after drying in 2 per cent citric acid; but it has no fertilizing value worth speaking of. The phosphoric acid precipitated as bone phosphate must therefore be looked upon as lost.

Now, it is clear that it would be much easier to avoid the formation of bone phosphate if a sodium-hydrate solution, distributed in jets, were employed as the precipitant than if milk of lime was used, since in the latter case we get particles of solid calcic hydrate, round which the solution easily becomes alkaline.

Experience also proves that in employing sodium hydrate, which is added until the phosphate solution remains very slightly acid or only just neutral, bicalcic phosphate can be precipitated so completely that only 0.1 to 0.2 per cent of all the phosphoric acid remains unprecipitated, while 98 per cent of the phosphoric acid in the bicalcic phosphate is soluble in citrate, and thus only 2 per cent of the phosphoric acid is present as bone phosphate.

The precipitated bicalcic phosphate, which is microcrystalline, is filtered off, washed and dried. It thus forms a light, pure white powder, and its proportion of citrate-soluble phosphoric acid amounts to 35 to 38 per cent., according to the completeness of the drying.

If we call to mind that about 2 per cent of the phosphoric acid in the raw phosphate is left behind in the extraction, that no quantity to speak of remains unprecipitated, and that about 2 per cent is recovered as precipitated bone phosphate, we shall find that about 96 per cent of all the phosphoric acid in the raw phosphate is extracted in the process as valuable citrate-soluble phosphoric acid.

The bicalcic phosphate obtained shows, even if it contains iron and aluminum phosphate, no falling off of soluble phosphoric acid, which is simply due to the fact that it can be perfectly dried, after which no conversion can take place. On the other hand, as we know, deterioration shows itself in damp acid phos-

phate. The following analyses may be quoted to show that such degeneration does not occur:

	Total P_2O_5%	Citrate-soluble P_2O_5%	P_2O_5 in % of total P_2O_5
Fresh	35.45	34.58	97.54
After 3 months	36.02	35.13	97.53
After 6 months	36.54	35.72	97.95

From the filtrate of the bicalcic phosphate is precipitated, as we have already mentioned, the lime that remains in the solution, together with the rest of the sodium hydrate solution, after the latter has been saturated with carbonic acid from fuel gases as carbonate of lime, which can be used as a fertilizer or in chemical workshops.

Its mass corresponds to about one-fourth of the weight of the bicalcic phosphate obtained, if the raw product used be free of carbonate. If calcium carbonate occurs in the raw product, the mass obtained in the process will be proportionately increased.

POWER EXPENDITURE.

From the statements given above it is easy to calculate what electric horse-power (direct current) produces per year of $350 \times 24 = 8{,}400$ hours; it will work out at 2.24 tons of bicalcic phosphate with 35 per cent of citrate-soluble phosphoric acid, if free of carbonate. If a 38 per cent article is produced.

$$\frac{2.24 \times 35}{38}$$

= 2.06 metric tons per horse-power year will be obtained, etc. The production with carbonaceous raw product has been stated above.

VALUE OF BICALCIC PHOSPHATE FERTILIZER.

Careful experiments extending over many years have been made, partly by Professor H. G. Söderbaum, agricultural chemist at the Central Institution for Experimental Agriculture, Stockholm, partly by Dr. Hj. von Feilitzen, director of the Swedish Peat Society, Jönköping, Sweden. Professor Söderbaum's earlier investigations are reported in "The Experiment Station Record," edited by the United States Department of Agriculture, Washington, Vol. XIV., No. 10, pp. 951-2 (1903), and he has also summed up the result of his investigations under the title of "Vegetationsversuche mit gefälltem Calciumphosphat" in the "Zeitschrift für das landwirtschaftliche Versuchswesen in Österreich," 1908, pp. 506-510. Dr. von Feilitzen has communicated the chief results of his investigations in the "Journal für Landwirtschaft," 1910, pp. 33-43.

As Dr. von Feilitzen is going to give an account of his further investigations at the congress, I will here only briefly mention the chief result of his and professor Söderbaum's culture trials.

The result of the experiments in cultivation is that the citrate-soluble phosphoric acid in the bicalcic phosphate proves to possess the same fertilizing value as the water-soluble phosphoric acid in the superphosphate, and consequently the same value as a trade product. That result might, indeed, have been foreseen, inasmuch as it is probable that the superphosphate in the soil is rapidly transformed into bicalcic phosphate through the agency of the compounds of lime present there. This result is supported by the trials carried out by practical agriculturists, who are well satisfied with both the result of the phosphate and its qualities in general. Owing to its high percentage the freight charges are low for the valuable ingredient, and a very small amount need be manipulated by the farmer. It is in all other respects easy to handle, and does not damage the sacks in the least.

THE SUPERIOR ADVANTAGES OF THE ELECTROLYTIC METHOD.

The merits of the electrolytic method are as follows:

(a) It admits of the use of cheap, low percentage raw phosphate not available for the superphosphate nor available for the superphosphate industry.

(b) By it a phosphate containing 35 to 38 per cent of soluble phosphoric acid is obtained even from low percentage raw material.

(c) Freightage for a given quantity of phosphoric acid in the finished article is only about half that in the case of ordinary superphosphate.

(d) Retrogradation of soluble phosphoric acid when stored does not occur.

(e) The raw phosphate need not be reduced to a finely powdered state.

(f) Bicalcic phosphate can be employed as a fertilizer on all kinds of soil, even on sandy and boggy land.

(g) Bicalcic phosphate will be of excellent use in the manufacture of "complete fertilizers."

(h) Sacks are in no wise damaged by the product.

(i) The product is a finely divided white powder which is easily spread on the field.

The process is now being carried out in a small factory, the first factory belonging to the Difosfat Company, Trollhättan, Sweden.

The Imperial Ministry of the Interior has published data relative to the refining of petroleum in Germany during the years 1910 and 1911. During 1910, 42 plans were in operation, employing on the average 1,546 workmen; in 1911 there were 40 plants, employing on the average 1,679 workmen. The wages paid amounted to $508,599 in 1910 and $570,010 in 1911.

Consul Frank W. Mahin of Amsterdam notes that the Dutch raw-sugar factories produced in the 1912-13 season 310,000 tons, valued at $15,577,500. In the previous season 268,000 tons were refined. The average yield per acre is placed at $61. Twenty years ago the annual sugar production was only one-tenth what it is now.

SULPHATE PROCESS OF MAKING PULP AND KRAFT.*

The assumption that sulphate pulp is adapted only to the manufacture of wrapping and so-called kraft papers is a faulty one, according to opinions expressed by J. M. Iversen and A. V. Tracy-Gould. It has not been possible, these writers say, in an article contributed to the Pulp and Paper Magazine for May 15, 1913, to bring the process properly to the attention of pulp manufacturers in Canada or the United States, owing to the fact that there are but a few experienced men who thoroughly understand it.

The majority of pulp men in Canada and the United States are ground wood pulp or sulphite pulp men, and therefore it is natural that those two systems are most widely known and used. Looking over the literature of pulp making, we find lengthy articles on sulphite, soda and ground wood pulp, the authors say, but hardly ever articles on sulphate pulp. This process is, so to speak, an unexplored field and it is fitting that more attention be given it by pulp and paper men. Sulphate of soda pulp will not replace the sulphite; but for the finer grades of paper and for wrapping it will undoubtedly force its way to the front.

There are many reasons for this, chief among them being the economy in maintenance and lower overhead expenses, lower demand upon power and the adaptability of any kind of wood. The demand for paper of quality that will stand all kinds of wear and tear, being at the same time durable, is enormous, and no pulp is more adapted for this than sulphate of soda. Besides the best grades of paper that can and are being manufactured, imitation silk and other articles of commerce of unlimited variety can be manufactured of this pulp at a lower cost than of sulphite. There is no doubt that in the case of sulphite there always remains in the pulp a small quantity of acid, which cannot be washed out and which, in time, has a deleterious effect. This drawback does not exist with the sulphate of soda process.

There has been considerable discussion as to what wood is best adapted for manufacturing sulphate of soda pulp and what kind of timber generally can be used.

Spruce and the pine, in the order named, are, without doubt, the best; but at present, where there is such a big demand for pulpwood, the other species of coniferous trees have been much used and it has been found that the results are exceedingly satisfactory.

It is usually understood that the woods in the order here named are to be preferred for sulphate of soda pulp manufacture, either because of the quality of the pulp derived from the wood or having regard to cost of manufacture; 1, spruce; 2, pine; 3, fir; 4, pitch pine; 5, hemlock.

It has been found by experience that the most economical length of pulpwood is 4 ft., not less, as this gives considerably less waste in sawdust and slivers.

Logs of an average of 8 in. diameter are regarded as having the most suitable fibers. Of course the difference in quality of fibers of 4 in. or 12 in. logs is very slight and practically should not be considered. The point that is to be more considered is the question of the quantity per cord, with the 8 in. logs giving the largest cubic contents.

One of the most important items in getting the chips is to see to it that the chippers and crushers are properly arranged, so as to make them work uniformly, also the question of having the knives of the chippers properly adjusted and kept continually sharp, to which, in the majority of cases, insufficient attention is paid. The size of chips should not be less than 1⅛ ins.; the longer the chips are the less loss in length of fiber; but from merchanical reasons it never has been attempted to make chips of greater length; in some solitary cases attempts have been made with 1¼ in. chips, but it was found that the chipper knives could not perform a clean cut. Until such time as new mechanical schemes are devised to overcome the difficulty, chips of 1⅛ in. maximum size will only be used.

After the chips have gone through the crusher they are passed over the screens which are arranged in such a way that they separate the chips from all slivers, large knots and sawdust. This residue should be used in keeping up the melting furnaces of the recovery plant, a cheap fuel under the circumstances. It is of great importance that the chips be kept clean of all this residue and conveyed in that clean state to the digester bins. The less slivers and knots and sawdust are incorporated with the chips the better pulp is produced and the less liquor is required for dissolving.

In the matter of cooking the chips in digesters, 18 hours is the usual length of time from the initial filling of the digesters to the blow-off. The boiler pressure has to be at least 125 lbs. per square inch and superheated steam; in that state it is taken to the digester through the circulating injector, the man in charge being careful to see that all the cold condensed steam is run off continuously until the desired temperature is proportional to the pressure.

It usually takes three-quarters of an hour to fill a five-ton digester with chips and liquor. The steam is then let in through the injectors and the digester is kept at about 80 lbs. pressure, which is reached in about four hours after the superheated steam has been let in. This pressure is kept up for about two hours, subject to the decision of the man in charge, and afterwards is gradually reduced to about 60 lbs. and kept at that pressure until blow-off.

The blow-off of pulp from the digester takes place through one main pipe only, which is so designed that it works on a swivel principle and can be connected

*From Paper.

on to each individual digester, if there are more than one.

This principle of using one blow-off pipe only has been introduced by Mr. Iversen and proven to work exceedingly satisfactory.

Opinions as to what kind of digester is to be recommended for sulphate of soda pulp differ; the majority of experienced pulp men prefer the stationary in preference to the revolving digesters. The point against the revolving digesters is the steam inlet and the connection to blow-off pipe. The steam inlet in this case, passing through the revolving tap, supplies the superheated steam directly to the chips and this has a tendency to burn and discolor the fiber at the place of entrance. The revolving digester offers the difficulty of connecting one to the blow-off pipe; if the blow-off cock on digester is not brought exactly over the blow-off pipe, either another turn of the digester has to be performed, or in case of friction clutch same slowly released, which requires considerable time. The slightest difference in position of the flumes prevents the connecting up of the cock and the blow-off, also new packing has to be used each time the connecting-up takes place. A stationary digester offers the advantage of having the superheated steam passed first through the liquor by way of the injectors.

The usual capacity of revolving digesters is 2½ tons maximum; the capacity of stationary digesters is usually from 2½ to 5 tons. The latter capacity is used mostly for larger plants. This capacity has been found to give the most satisfactory and most economical results so far as manufacturing of pulp, installation and cost of plant are concerned.

It has to be considered that digesters for pulp by the sulphate of soda process are not brick-lined as in the case of digesters for sulphite. The soda not affecting the steel, it is left entirely unprotected, but these digesters have to be insulated properly on the outside just as in the case of boilers, to insure economy of steam consumption. The lining consists usually of an asbestos composition.

The cooked pulp and liquor is then blown off to the wash tanks, under a pressure of about 60 lbs., through a main pipe, which connects to a swivel pipe. These swivel pipes can be connected to pipes leading to the different wash tanks. Tanks must be water and air tight and have the pipe connection on the top of the tank. Besides the wash tanks, there is a tank installed, called commonly the save-all. This tank is connected on to the wash tanks by means of large suction pipes, which perform the duty of conveying off steam from the individual wash tanks; as the steam carries with it a quantity of pulp particles, these are deposited in the save-all tank, the condensed steam is either taken through the condenser to the hot water tank or allowed to escape through a relief pipe. The total capacity of the wash tanks should be the capacity of digesters plus 60 per cent and not less.

These tanks are provided with a spray pipe placed underneath the covering, which is circular and connected to a pipe which leads to the hot water tank, 125° Fahrenheit being the average temperature of the water.

The wash tanks are provided with a perforated galvanized steel plate, the perforations being preferably of conical section and placed about 1 ft. above the bottom of the tank. The hot water from the hot water tank is let in and by its own weight forces the liquor, which was blown off, together with pulp, into the wash tanks, through the perforated plates to the bottom of the tanks. After the tank is filled with water the supply is shut off and the pulp regarded as washed. The accumulated liquor at the bottom of the tank is forced to the next tank and enters at the top, replacing the liquor which the pulp of this tank is mixed with, this replaced liquor being forced on the same principle to the third tank. The washing process starts in tank No. 2 in the same way as in tank No. 1. From the third tank the liquor is conducted to a liquor storage tank.

The hot water tank is placed above the digesters, and near the bottom of the tank a spiral pipe is placed, which acts as a water heater. Steam from the blow-off of the digesters, from high to low pressure, is used for heating the water, also all condensed steam from save-all tank is pumped to this tank. Before the condensed steam is led off from the spiral pipes to the save-all, the turpentine should be removed, as it forms an important item of by-products in sulphate of soda pulp manufacture.

The liquor used in cooking by dissolving the tar in the chips becomes black and is conducted to the wash tanks and then let off to a tank below the wash tanks, hence the name of black liquor storage tank.

The washed pulp is dumped into a tank located underneath and to the side of the wash tank through a side opening. The tank is half circular and has an agitator for the purpose of mixing the stuff by having cold water added until it attains a uniform and thin consistence. From the stuff tanks the pulp is passed through a knot screen to remove all the big knots which remained undissolved in the liquor.

After passing through the screening process it is forced to a storage trough, where it is further diluted, after which it is conveyed to finer screens, which separate the rougher fibers and convey the finer fiber to the decker or wet machines, and from the deckers to storage chest, then to kollergangs or beaters.

The rougher fibers are treated in refiners and returned to the screens, from which it passes through the same process as noted regarding finer fiber. So far this description has dealt purely with the mechanical end and the different stages of transition of the woodpulp.

We will now deal with the chemical side of kraft pulp making.

Referring to chemical solutions used, we have mentioned the white and black liquor. We shall describe

what is understood by white liquor and its chemical composition. The white liquor is composed of sodium sulphate, commonly called salt cake, which, dissolved in proper proportion, mixed with solution of chloride of lime, composes caustic soda. Roughly, the proportion is 75 per cent of salt cake and 25 per cent of lime. This solution acts as the agent in dissolving the wood chips into fibers and ultimately into pulp. (This explanation of the composition of "white liquor" is not at all informing, even to a chemist.)

Since it would be commercially impossible to manufacture pulp on this principle without resorting to means of recovery of this main chemical, apparatus is installed to recover the soda from the liquor.

The white liquor, acting upon chips in course of cooking, combines itself with the tar of the chips, passes to the wash tank and from these is forced to a storage tank, from which it is pumped to the measuring tank, as previously mentioned, located above the digester, and used over again in digesters in proportional measures with white liquor for cooking. This liquor being of dark brown color, the name of black liquor has been applied to it. About 80 per cent of this solution is passed through a process of elimination of all the impurities and leading to the recovery of soda. This liquor is passed from the storage tanks to an economizer, which evaporates part of the water in the black liquor, and is then let into a storage tank located above the evaporating plant. This plant consists of wheels with discs arranged in such a way that they shape themselves like the thread of a screw.

They are placed one behind the other in circular troughs, which are connected by a channel. These wheels are right and left and when placing them into troughs care should be exercised that a left make wheel should follow a right make wheel or vice versa. The liquor, after passing through the economizer and stored in storage tank, just mentioned, is conveyed into the troughs of the evaporating plant. The disc wheels keep the liquor continuously moving and so assist in evaporating part of the water contained in it. The heat required for evaporating is the over supply of heat from the melting furnace, which will be described in due course. After the liquor in the evaporating plant has acquired a certain thickness, approximately the thickness of linseed oil, it is run off by means of pipes into a revolving furnace, where it is again exposed to the over supply of heat from the melting furnace and by this means all the water is evaporated from the substance. Since the opening of the revolving furnace at the evaporating plant is smaller in diameter than at the end next to melting furnace, all the substance from which water has been evaporated overruns the larger opening and deposits itself on top of the melting furnace in the shape of clumps and ashes; this substance is black in color containing tar and wood size, and is commonly called the black ash.

It is well mixed with a certain quantity of saltcake and deposited in a hot melting furnace, where it is gradually exposed to a high temperature reaching 3,000° Fahrenheit; this temperature is reached by means of forced air draft.

This attained heat meets the black ash and purifies the soda from all tar, wood size and other impurities. The melted soda is run off into a tank, placed below the furnace, which is filled with hot water, where it dissolves. This tank also receives the weak white liquor, which will be described later on. To help to dissolve the melted soda and to keep the solution uniform, agitators in shape of propellers are continuously keeping the solution in motion. To prevent undissolved particles of soda from reaching the pump a screen is placed about 2½ ft. from the outlet at the tank.

The tank is covered with a cover plate, having a sufficiently large opening to allow the melted soda to run into the tank. This cover is for the purpose of preventing the solution in the tank splashing over the sides, which is apt to happen owing to the difference in temperature of melted soda and water. The steam generated by the mixing of the melted soda is carried off through a stack out to the air.

The soda solution is forced, by means of a force pump, to the caustic soda tank. Special open steel bar baskets are suspended on the inside of the tank which are filled with lime. This gradually dissolves in the soda solution, and to hasten the mixture and make same uniform, agitators are installed, which keep the liquid continuously in motion. While the mixing is taking place, its temperature is maintained close to the boiling point. After thorough mixing the agitators are stopped and the solution called strong white liquor is allowed to stand until all undissolved particles of lime and impurities have settled at the bottom of the tank; then the clear liquor is drained off to a storage tank, placed below and to the side of the caustic soda tank.

After all the liquor has been drained off the caustic soda tanks are filled with water, the agitators started again; after the rest of the lime has been dissolved, the agitators are brought to a stop again, the solution allowed to stand to clear and this weak caustic soda solution is drained off to a tank placed underneath.

The process is followed up two or three times and the weak caustic soda solution obtained drained off to the same storage tank.

By this time all the strength has been taken out of the lime, and the remaining limestone and impurities are then removed from the tank by means of a valve placed at the bottom of it. These undissolved particles drop down into the filter tank and there they remain until all moisture has drained off and all slack lime, sand and other impurities have dried; they are then removed as being of no further value to the mill.

In a mill of large capacity it would be advisable to burn the slack lime and use it over again for the purpose of making caustic soda.

The weak white liquor, which is obtained, as stated before, from the second and succeeding wash, is then

run off into the dissolving tank at the recovery plant, there to be mixed with the melted soda from the melting furnace.

Regarding the recovery of soda from the black liquor, experience has shown that about 90 per cent of soda of the sulphate salt cake used can be recovered, the loss amounting practically to 10 per cent only; this loss has to be made up by adding the necessary quantity of salt cake to the black ash in the melting furnace, as stated before. Good quality of salt cake contains only 3 per cent of impurities. Care has to be taken that the sale cake is kept perfectly dry in storage and that it is always kept in powder form; any moisture tends to cake the powder, which is very hard and difficult to break up, and before it ever reaches the melting furnace these cakes have to be pulverized.

With regard to lime, care also has to be exercised that it is kept in a perfectly dry condition; no large quantities should be stored, as the exposure to air, which contains certain moisture, slacks it and so reduces its strength. If lime is stored for any time it will lose its original strength to such an extent that double the quantity has very often to be used in the process.

The liquor of the sulphate of soda process in the manufacture of kraft pulp is the only known agency which readily dissolves the bark and small knots. There is no necessity of installing barkers as in the case of unbleached sulphite, soda and ground wood pulp. This of course applies to kraft pulp, but in the case of bleached sulphate of soda pulp barkers have to be installed.

Sulphate of soda pulp can be manufactured for the highest grade of bleached pulp. Bleached sulphate of soda pulp is of higher quality, so far as strength is concerned, than bleached sulphite pulp.

After being turned into finer grade of paper, such as bond, money paper, etc., it retains its uniform strength under all conditions, never breaking, and even if exposed to air and sunlight does not turn yellow, as is the case with paper made of bleached sulphite. Where strength, durability and color retaining qualities are concerned, paper made of sulphate ot soda pulp is far superior to any other kind of pulp, except rag pulp, which stands on the same level of quality.

Ground wood pulp, mixed with bleached sulphate of soda pulp, in lesser quantity than that required with sulphite can be manufactured into the best quality of book paper.

The bleached sulphate of soda pulp can be manufactured cheaper by at least 10 per cent than the high grade sulphite pulp.

In regard to initial cost of installation of a sulphate of soda pulp mill, this is about 25 to 30 per cent higher than the cost of installation for equal capacity of a sulphite mill, but considering that no acids are used in the process, therefore all piping, tanks, etc., are made of steel or iron, and no brick lining of digesters is necessary, the cost of maintenance of such a plant is reduced to a minimum, which compared to the expenditures on maintenance of a sulphite plant of equal capacity, shows up very favorably, and in course of a few years easily equalizes the expenditure and proves to be more economical in the course of years.

Pulp and paper manufacturers will do well to consider the sulphate of soda process. There is no doubt that, sooner or later, it will play an important part in the manufacture of the finer grades of paper where durability and retaining qualities are regarded as primary requirements.

MANUFACTURE OF CALCIUM CARBIDE.*

The commercial manufacture of calcium carbide, credited to Willson in America, and to Herould in Europe, started in the early eighties, and by progressive development, has risen to become a consumer of electrical energy greater than any other electric furnace process. As is the case with all new industries, the beginnings were crude and inefficient. At present, although the proposition presents problems of some magnitude, the average of excellence is high, and the operation of numerous works is successful, from a commercial standpoint. The steadily increased demand for carbide resulted in increased size of furnaces, together with the electrical transformers necessary to their successful operation. The manufacturers of electrical apparatus have, therefore, been forced to design and build generators and transformers specially adapted to the need of electrical smelting.

The raw materials used in the manufacture of calcium carbide are lime and some form of carbon, such as anthracite coal or coke. Both these materials should be as pure as possible, special attention being paid to their freedom from phosphorus. Sulphur, magnesia, silica, iron and alumina should be present in small quantities only.

Phosphorus occurs as calcium phosphate, which is reduced at the temperature of the electric arc, and in the presence of carbon, to calcium phosphide, which when brought into contact with water, gives off phosphoretted hydrogen. This gas mixes with the acetylene, and when burners are lighted, causes a haze of phosphorus pentoxide, which is very objectionable. So carefully, however, are the raw materials selected, that today all commercial carbides are practically free from phosphorus, the average content of phosphine in acetylene being less 0.002 per cent by volume.

Sulphur, unless present with considerable amounts of alumina, has little influence in the carbide. Calcium sulphide formed in the furnace by the reduction of calcium sulphate, does not decompose in the water. In the presence of alumina, aluminum sulphide may be formed; this yields hydrogen sulphide when brought into contact with water. Practically speaking, very little trouble is experienced with sulphur, in-

*From the Journal of the Society of Chemical Industry.

asmuch as the lime and coal used rarely contain a prohibitive quantity.

Magnesia has the peculiar property of interfering with the formation of calcium carbide in the furnace. If more than 1 per cent of magnesia be present in the lime and coal, the electrical energy required becomes noticeably so much greater, that such raw material is considered unfit for use. To counteract its effect a flux of fluorspar has been recommended by some authorities. In the experience of the writer, this is not very successful. It is well known that magnesia mixed with carbon and treated in the electric furnace will not form a carbide, and is highly infusible, even at the highest temperatures obtainable. Metallic magnesium heated in a current of acetylene, however, readily forms magnesium carbide.

Barium and strontium form carbides with ease when their oxides or carbonates are reduced under similar conditions with carbon at electric furnace temperatures.

Silica, iron oxides and alumina form silicates, aluminates, and ferro-silicon, which reduce the purity of the carbide, and its output from the furnaces.

The presence of *water*, either in the free states in the coal or combined as hydroxide in the lime, is the greatest difficulty the carbide maker has to contend with, as it reduces the furnace output more than any other factor. For this reason, the coal is thoroughly dried, usually in a rotary coal—or gas—fired dryer. The lime should be burned in kilns at the carbide works, and fed direct to the electric furnace to secure the best results.

The Preparation of the Charge for the Furnaces. The lime is roughly crushed to pieces of one-inch size, the coal, thoroughly dried, to above pea size. They are then roughly mixed in about the theoretical proportions called for by the equation, $CaO+3C=CaC_2+CO$, or approximately 100 parts by weight of the lime contents of the lime to 65 parts of the carbon contents of the coal or coke.

In the early history of the industry it was believed necessary that both the lime and the coal should be ground very fine, and thoroughly mixed, in order to secure uniform results in the quality of the carbide. This fine grinding, however, caused the furnace to blow out large quantities of dust, which upset the proportions of the mixture, frequently producing very irregular results. With experience in operation, and particularly with furnaces of increased size, the fine grinding was abandoned, until at the present time lime as large as eggs is used in some furnaces; the coal, however, is kept about ¼-inch mesh. In this way the dust losses from the furnaces are decreased to a minimum, the actual output and quality of the carbide being at the same time improved. In other electric furnace processes the same change has been affected, and the prevailing practice is to use coarsely ground raw material, which offers little resistance to the free escape of the furnace gases.

Electric furnaces for the manufacture of carbide can be divided into two types, the ingot furnace, in which the carbide is allowed to solidify, and the tapping furnace, in which the product is run in the molten state in the same manner as iron. At first, carbide was made entirely in the ingot furnaces, on account of the difficulty of attaining a temperature sufficient to melt it thoroughly.

The simplest form of ingot furnace is the Borchers, or pot furnace, in which some form of iron crucible is lined on the bottom with a layer of carbon, this being connected to one side of the electrical circuit. The other terminal of the circuit is connected to a carbon rod held in a suitable holder, which is suspended vertically in the center of the crucible, and adjustable up and down within it. To accomplish this, some form of hoist is used, as these carbon rods and holders are heavy, weighing sometimes nearly a ton. To start such a furnace, the moving electrode is lowered to contact with the carbon bottom forming an arc; the mixture of lime and coal, previously prepared and usually stored in a bin above the furnace, is fed in around the arc and entirely covering it. An ammeter in the circuit indicates the current used, and the hoist is raised or lowered, often by automatic relays, to keep the current at a constant figure. The early Willson furnaces used in America used a current of 2,000 amperes and 75 volts. The arc so started and burned in the charge smelts a pool of carbide, which gradually deepens, necessitating frequent lifting of the electrode, until the crucible is filled. The crucible is then wheeled out, and an empty one substituted. When sufficiently cool, these crucibles were dumped on a grating, the unconverted mixture going through the grates to a recovery storage bin, and the ingot itself taken to a clearing room. Here the crust or scale was removed by the use of axes or pneumatic tools. This process was unsatisfactory from the standpoint of uniform quality of lime and coal surrounding the ingot was unconverted, and therefore had to be rehandled. A considerable quantity of coal was burned out in the operation of dumping the pots, necessitating further addition of coal before the mixture could be used again. In practice four tons of raw material were handled to make one ton of carbide. The ingot itself varied from almost pure carbide in the center, where the heat of the arc was greater, to an outside layer of melted lime and coal which had not become sufficiently hot to be converted into carbide. The removal of this outside layer was often difficult and frequently the crust was found in the carbide, causing much dissatisfaction.

At this stage the American makers began to use a very ingenious furnace to offset these difficulties. This is known as the Horry rotary furnace, and while still adhering to the ingot principle, it has been so perfected, both in operation and efficiency, that it competes successfully with any other process.

The body of the furnace is formed like a spool with wide flanges fastened to the drum, thus forming with

it three sides of a square if viewed in cross section. The fourth side is formed by removable plates, which are clamped across the ends of the sides or flange plates by use of bolts or clamps. Two electrodes, suspended from above, hang vertically in this square space. There is no electrical connection made to the furnace itself, the current passing from one electrode to the bath of carbide, and through the carbide to the second electrode. The furnaces are therefore known as two-electrode single-phase, and use a current of about 4,000 amperes at 75 to 80 volts. In operating this furnace, a small quantity of broken coke or carbon is placed under the electrodes, the arc sprung, and the charge of lime and coal fed in until the arcs are well covered up. The electrodes themselves are fixed, the regulation being accomplished by slowly revolving the drum away from the arc as the carbide accumulates in a pool beneath the electrodes. This regulation is automatic, being controlled by a relay which engages a pawl to increase or decrease the current by revolving the furnace to the right or left. The revolution of the furnaces is very slow, the movement at the circumference being about 6 inches per hour.

The ingot so formed passes slowly downwards from the electrodes under the axle of the furnaces and upwards at the back. In the rear the end plates are unbolted and the carbide ingot exposed. Holes are drilled across the ingot by compressed air drills with water cooled points, the water cooling the carbide and slaking it in front of the drill. Into the holes so formed, wedges are driven and a section of the ingot broken off and carried away by a crane to the cooling room.

The operation of these furnaces is continuous during the life of the electrodes, which, being kept well buried in the charge, are consumed very slowly. The actual fusion of the carbide extends very close to the cast-iron sides of the furnaces, thus minimizing the quantity of unconverted charge and crust.

Two other electrode furnaces having a crucible instead of the revolving wheel are also in use. These differ in principle from the rotary furnaces only in not being continuous, the crucibles being changed when full, and new ones substituted every 10 and 12 hours.

The Tapping Furnace.—In Europe the early pot furnaces of the ingot type were slowly changed to tapping furnaces, in which the carbide was heated to sufficient temperature to run out in the molten state into cast-iron moulds. The type of furnace used was much the same as the ingot pot furnaces, with a single electrode suspended in the centre of the pot, which latter was lined at the bottom with carbon and provided with a suitable connection to the other side of the circuit. One of the greatest difficulties to contend against was actual maintenance of the carbide at a temperature at which it could run readily from the furnace. To meet this a flux of lime was added which increased the fluidity, but somewhat reduced the quality of the carbide.

With the developments of larger transformers larger furnaces were built. Also skill in the art of tapping the furnaces played no small part in their ultimate success. At the present time, carbide is tapped easily at the highest temperature, and the grade of the material so made is fully equal to the best ingot product.

Later developments in tapping furnaces tend towards two or three electrodes suspended vertically in the furnace, using two—or three—phase current to distribute more equally the load to suit the necessities of the generating plants. Such furnaces can be built to large sizes of 2,000 to 3,000 h. p. and even more, with great economy gained from the labor and power standpoint.

The manufacture of suitable furnace electrodes has been the deciding factor in many cases. Often manufacturers of carbide were unable to use furnaces because no satisfactory electrodes could be had. In 1892 the only satisfactory electrode made in the United States was 4 inches square, and would carry about 500 amperes. Today, electrodes 18 inches to 22 inches are in the market, which are satisfactory and reliable. Even larger electrodes are advertised capable of carrying very heavy currents. Electrodes made by assembling a number of 8-inch diameter units in parallel in a single head or holder, have been in successful use at Shawinigan Falls for a number of years. Currents up to 40,000 amperes are occasionally used, with 25,000 to 30,000 amperes the average load.

With reference to the use of graphitised electrodes, there is a great difference of opinion, the ingot makers using graphite, whereas those using the tapping process prefer the amorphous carbon electrodes. The writer, in using both, found that the graphite consumed too rapidly in the tapping furnace, making the cost prohibitive, so the amorphous carbon electrodes were adopted on account of their cheaper price. This is easily understood when it is considered that the ingot makers use an excess of carbon in the furnace charge, while the tapping furnace requires a slight excess of lime.

Whether the carbide itself is made by the ingot or tapping process, its subsequent treatment is much the same. The ingot carbide possesses the disadvantage of having to be freed from scale or crust.

The problem of crushing and sizing is one of successive reduction through crushers and rolls, making the least possible dust. Ingot carbide has a natural tendency to break into cubes on account of its crystalline structure caused by slow cooling of the ingots. Tapped carbide, on the contrary, is cast at approximately 2,500°C. into a heavy cast-iron chill, and is consequently close grained and dense. It is much harder to break and requires very strong machinery. For the first breaking, jaw crushers of the Blake type are common, although some makers prefer gyratory crushers. For granulations of carbide to sizes of ¼-

inch to ⅛-inch, low speed rolls are used, as these machines make the minimum amount of dust. The sizing is usually done on trommels or rotary screens, which deliver the product in sizes varying from large lumps, 8 inches by 4 inches, to fine materials, 16 by 30 mesh, suitable for a certain type of table lamp.

A can-making plant is a necessary part of every works, where steel and tin air-tight receptacles are turned out in large quantities to hold the carbide. The standard packages in use hold 100 lbs., 110 lbs. and 220 lbs. net weight of carbide. Small tins containing from 1 to 25 lbs. are also filled to suit the trade for automobile lamps, etc. All carbide which is exported by water is subject to rigid insurance rules, which necessitate the steel drum being cased in wood. A complete installation of box and stave-making machinery is therefore part of the equipment of every export works.

The largest use for carbide is in the generation of acetylene for lighting purposes, and this business steadily advances from year to year, showing the satisfaction that is experienced in the use of this beautiful light. The oxy-acetylene blowpipe is becoming a common tool in well-equipped shops, and in the hands of skilled operators gives great economy in repairing broken parts and in cutting away unnecessary metal. The cyanamide industry in Europe is believed to be on a sound financial basis, and is now using thousands of tons annually. The decomposition of the cyanamide and the formation of ammonium sulphate has also been undertaken.

On May 17 the Cuban government put in force new and comprehensive public-health laws (Ordenanzas Sanitarias) which were contained in executive decree No. 530, May 13, 1913. These laws cover the whole domain of public health and sanitation. Chapter 2 (arts. 8-47) is devoted to pure-food regulations and deals with such topics as adulteration, preservatives and coloring matter, substitutes and compounds, labeling, standards of purity and containers. Among the other subjects treated in the laws are water supply and sewage, construction and care of premises of public and private buildings, markets, hospitals, factories and shops, slaughter houses and cemeteries.

Reuter's correspondent at Georgetown, British Guiana, reports that experiments in the cultivation of hedychium (known locally as the ginger lily), the areca nut palm, and the castor-oil plant have been decided on by the Board of Agriculture. All these products are at present to be found in the colony, but so far they have never been of any commercial value, and the idea now is to ascertain to what extent they may be reckoned upon in the improvement of the industrial conditions in keeping with the avowed policy of the present administration.

PRODUCTION AND INDUSTRIAL APPLICATION OF BY-PRODUCT COKE OVEN GASES.*

By J. BECKER, and L. B. ROBERTSON.

In a paper covering the production and industrial applications of coal gases you will all appreciate that this subject can be treated only in a general way, without taking up more than the allowed time. We shall therefore attempt to briefly outline the process of distillation of coal and the treatment and application of the resulting gases.

The first distillations of coal were performed in beehive ovens for the purpose of making coke. No gas is recovered from this coke-making process, and the only application of the gas produced is its combustion in the beehive oven over the coal in order to supply the heat and maintain the temperature necessary for the coking process. Then coal was distilled in retort ovens, for the recovery of illuminating gas. Coal is charged into these retorts and the liberated gas collected in a so-called hydraulic main. The gas next passes through a washing and purifying system and is collected in gas holders from which it is distributed to consumers, either for illuminating or household purposes. These retorts vary in size as well as in their position in the retort benches; horizontal, vertical and inclined retorts are in present use; the coal coked in these retorts must be of a very high grade, in order to produce the best gas. Usually the desired candle power of the gas governs the quality of the coal to be used. The fuel necessary to perform the distillation of coal consists of a part of the coke produced by this gas-making process.

The first chamber ovens were waste heat ovens, and, like beehive ovens, were built for the sole purpose of producing coke from coal. We call them chamber ovens to distinguish between this type and other types of ovens and retorts. The chamber oven is built in the form of a long narrow chamber varying in size from 4 to 15 tons' capacity. The division walls between these chambers contain flues in which the gas produced from the distillation of the coal is burned so as to maintain the temperature necessary for the coking process. The gas received from waste heat ovens passes through openings in the top of the oven chambers and from there burns downward through the flues. Air necessary for the combustion of this gas is admitted from the outside. The waste gases from these ovens have a high temperature and are often utilized under waste heat boilers for generating steam.

There are also built, especially in England, the Mond Gas producers. Low-grade coal is charged into these producers and the gas received is used for heating purposes after recovering the ammonia and

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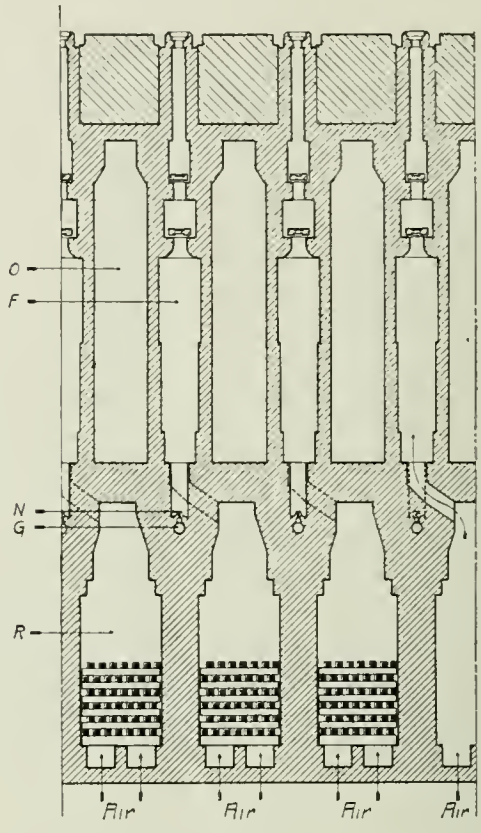
tar. A large amount of steam is introduced in order to keep the gasifying zone at a low temperature to prevent decomposition of the ammonia formed. The amount of ammonia recovered from this process amounts to about 20 to 80 pounds in form of ammonium sulphate. The recovery of the by-products makes this process a very economical one.

Competition, and the desire to produce gas and coke most economically, brought an oven on the market, which, we are sorry to say, is not by any means used enough in this country at the present time for making gas and coke. This is the By-Product Coke Oven. Long ago the wasteful bee-hive ovens disappeared from the plants of the coke and gas manufacturers in Germany. The by-product coke or gas oven is a chamber oven with a capacity of about 5 to 15 tons of coal per oven chamber. These ovens are built in batteries varying from 25 to 70 ovens per battery. The division walls between the ovens serve as heating walls and contain either vertical or horizontal flues in which the combustion of the gas takes place. In the improved by-product coke and gas ovens, the air used for the combustion of the fuel gases is preheated in recuperators or regenerators placed under the oven chambers. The products of combustion of the fuel gases first pass through the recuperators or regenerators in order to heat them and are then collected in a larger flue and discharged through a chimney.

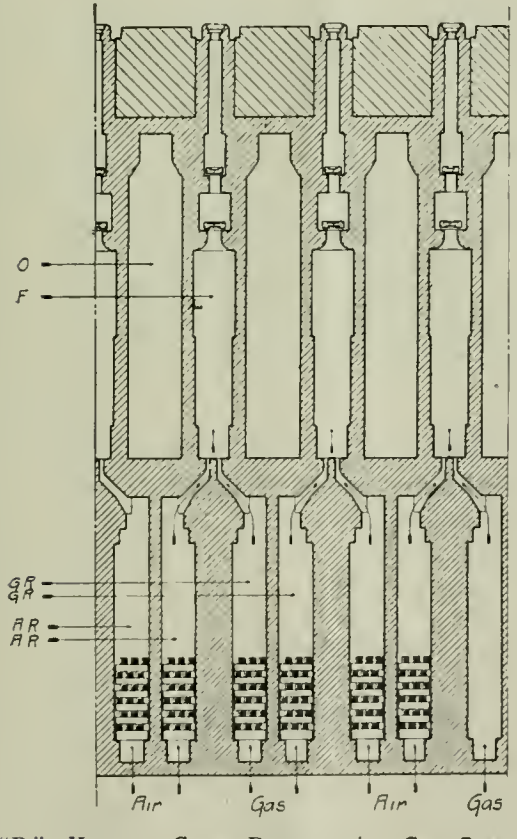
In explaining the process of coal distillation we shall confine ourselves to the chamber oven. The kind of coal to be used depends entirely upon the purpose for which the coal is being coked, whether for the production of gas only, coke only, or both coke and gas. At coke plants, the coke is considered the main product. At gas plants, gas is the main product, and the coke is considered as a by-product. The ideal way would certainly be, to consider both coke and gas as main products, which means making good gas and good coke from a given coal. All this may be done in a chamber oven only, by coking certain coals or mixtures of certain coals. The chamber oven can produce a good illuminating gas as well as a valuable furnace coke, while retorts can produce a good gas but an inferior coke which cannot be used for blast-furnace purposes. The gas manufacturers must use a coal which gives a gas with a certain candle power. It is an undeserved handicap to the gas manufacturer to make gas on a candle power basis, since most of the gas is burned in mantles where the candle power of the gas means little or nothing. For this reason the quality of the gas should be judged on a B.t.u. basis. The Germans have long ago abolished the system of selling gas with a given candlepower. The requirements are certain heat units per cubic meter. Americans, considered as the most progressive people on earth, will undoubtedly do away with this antique law of judging qualities of gas by candle power. If this requirement is done away with, gas, with a good heating value, could be made with an inferior and cheaper kind of coal, which means that gas could be sold cheaper for public service. In order to bring this about, Americans should continue their progress by adopting the mantle universally, which will allow a lower candle power gas to be used.



"A." Koppers Cross Regenerative Coke Oven.

In the process of distillation, coal is charged into the chambers and the heat for coking this coal is transmitted from the heating flues to the coal charge. The gas evolved from the coal is conducted by means of ascension pipes to the collecting main and from there to the cooling, washing and purifying apparatus by means of an exhauster which forces the gas through the pipes and apparatus into the holder. Immediately after the coal is charged into the oven, coking begins, forming a solid and thick mass on the surface of the coal. This mass on the outside of the charge consists of partly decomposed coal which is heated by radiation from the heating wall. The reversed side of this mass, that is, the side towards the center of the coal charge, is cooled by the coal which lays just behind it. The tar formed from this mass condenses, on account of the cooling effect of the cooler coal behind it, and is redistilled again as the heat travels towards the center of the charge. The coal in the center of the oven stays unchanged until the tar mass has traveled towards the center and in turn is decomposed after it has reached the necessary temperature. In other words, the tar travels in or condenses toward the center of the coal charge, and the gas passes out toward the oven walls and from there

along the walls to the ascension pipes. This means that the temperature of the coal in the center of the charge may be very low for many hours, and that this temperature will not raise appreciably until the heat introduced through the oven walls has reached the center. The fact that the tar condenses toward the center of the charge, forming there a tight and solid mixture of coal and tar, proves that the gas must travel from the coal charge through the coke formed, to the walls, and that the gas does not pass through the coal mass; in other words, the gas travels in the opposite direction to the flow of heat. Tests were made on coke ovens in Germany, where coal was coked at a coking time of 30 hours. The coal was charged wet. The temperature of the center of the coal mass did not exceed 100° C. after 15 hours' coking. This proves that the action of the heat is not to evaporate the moisture in the entire coal charge first, but is simply to evaporate the moisture of the coal nearer the walls, which moisture condenses toward the center of the mass and gradually evaporates as the heat travels to the center of the coal charge. The moisture remains in the coal during the first period and assists in the gradual condensation of the tar first formed. This is one reason why some coal



"B." Koppers Cross Regenerative Gas Oven.

when charged wet will give a better coke than when charged dry, for the moisture condenses the more heavy tar in the mass, which, after being redistilled, gives the coal the desired bonding substance to form good coke. This may possibly reduce the amount of tar somewhat, but, due to the redistillation of the tar leaving its carbon, an increased coke yield will be obtained. The amount of gas as well as the amount of coke produced by this process is greater than in retorts.

If a given coal is coked in a retort and in a chamber oven, the results will be that from the retorts will be obtained a larger amount of thick, inferior tar containing a high percentage of free carbon and a smaller amount of coke, on account of the carbon which forms on the roof of the retorts, whereas in the chamber oven a larger amount of coke and a smaller amount of light and fluid tar, containing a small percentage of free carbon, will be produced. The gas received from both is in quality practically the same, but the quantity is larger in a chamber oven. The amount of gas produced in the chamber oven is the maximum which can be obtained.

The greatest difference in the principles of the distillation in chamber ovens and in retorts is, that by coking small amounts of coal as is done in retorts, the condensing and redistilling of the tar which takes place in the coking process of chambers does not occur in the retorts. The first formed tar gases cannot condense, but pass along the roof of the retort where they are decomposed, leaving a large amount of carbon as residue. Part of the carbon formed by the decomposition of these tar fumes is carried with the gas into the hydraulic main, where it settles out and becomes mixed with the tar, thus increasing its per cent of free carbon. In a retort, it is quite necessary to have considerable overhead heated surface, which is the roof of the retort, in order to produce a good gas yield. If this decomposition of the tar gases did not take place, the yield of the gas in the retort would be very low. The residue from this decomposition, the carbon found on the roof of the retort, is recovered in a chamber oven in form of coke, which has some value.

The manner in which the heat is transmitted to the coal charge, as well as the temperature in the heating flues, has a great effect on the quality and quantity of the coke. Coal coked at high temperature usually gives a higher coke and gas yield but a lower by-product yield. The gas received from coal coked at a high temperature, which means in a short coking time, usually gives a gas with a lower candle power, but there is not much change in the heating value per cubic foot. The heating value of total gas produced per pound of coal distilled is higher when coking the coal at high temperatures. The coke received from coking the coal at high temperatures is usually smaller in size than that received by coking at low temperatures.

In order to produce the most uniform coke and gas at any temperature of the heating flues, it is very important to have the heat in the heating walls distributed very uniformly. Thus, the rate of heat transmission to the coal charge is uniform and an even coking of the charge will take place. Overheated or

underheated spaces in the heating wall will show up in the quality of the coke. The coke nearer the overheated area will be of smaller size while the coke produced from the underheated area will be undercoked, which means that it still contains uncoked coal particles and consequently too much volatile matter. Overheated areas in the oven walls affect the gas passing over these areas by decomposing the heavy hydrocarbons in the gas thus decreasing the candle power. From the above it is easily seen that for coking coal, only that oven should be used in which the combustion of fuel gases and consequently the transmission of the heat to the coal charge can be controlled in every heating flue. An oven which has many of these flues per heating wall and one in which every flue can be controlled and regulated individually would be the ideal oven to make the most uniform coke and the best gas.

There is one great advantage of the coke oven over the retort. In a coke oven, illuminating gas can be made from a lower grade of coal than in retorts. Or, a high-grade gas coal, giving a poor quality of coke, can be mixed with a low volatile coal giving a high grade of coke. Such a mixture will produce a good coke, suitable for blast furnaces and foundries, and a good quality of illuminating gas. This is done by means of separating the gas received from the coking process. The gas given off from coal during the first 10 hours of the distillation has a higher heating value and a higher candle power than the gas produced towards the end of the process. The first gas may have 16 to 18 candle power and 650 to 700 B.t.u., while the gas received from the second part of the distillation may have 12 to 14 candle power and 560 to 600 B.t.u. These two gases are collected separately by means of two collecting mains, or by one collecting main divided by a longitudinal partition. Each gas passes through a separate washing and purifying apparatus. The gas received from the first part of the distillation, the so-called "rich gas" is sent to the rich gas holder, and that received from the second part of the distillation is burned under the ovens. The amount of each gas depends largely on the quality of the coal charged into the ovens. Also let us say here that ultimate and proximate analysis of a coal does not tell by any means what products would be obtained from the distillation. For determining the coking value of a coal as well as the quality and amount of distillation products, the coal must first go through a distilling process, either in a laboratory or by coking the coal in an oven chamber.

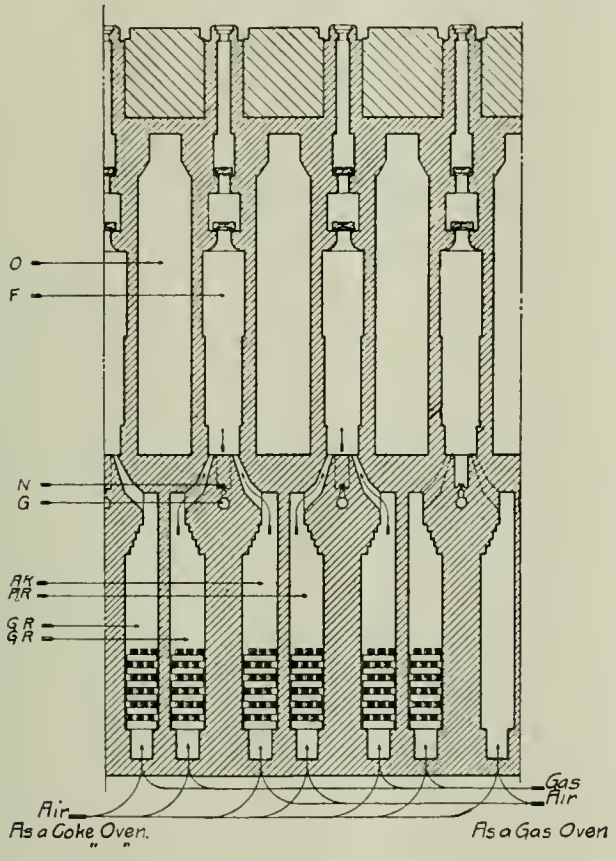
The first process installed for treating the gases was by cooling, washing and purifying. The gas, after leaving the collecting main, passes through a cooler, where it is cooled to about 80° F. The water produced from the coal both from the condensation of the moisture and the water formed from the hydrogen and oxygen of the coal, and the tar is condensed in these coolers. They are usually tubular, the water passing through the tubes and the gas around them. After leaving the coolers, the gas passes through a number of washers, where it is brought in direct contact with water, which absorbs the ammonia in the gas. The gas then passes through boxes containing iron oxide for the removal of hydrogen sulphide and cyanogen and then is led to the gas holder. During the last few years the methods for treating the gases have been very much simplified. It is easily understood that to wash out the ammonia requires an enormous quantity of water, especially in larger plants. Also the floor space taken up by the ammonia washers is enormous. The percentage of the ammonia recovered in these washers depends to some extent on the temperature of the water used. In summer time and especially in places where the temperature of the water supply is high, the washing of the gas is not perfect—losses of 10 per cent of the total ammonia produced are not unusual.

Being Koppers men, we wish to explain the direct process for treating gases. This process was introduced by the H. Koppers Co., in practically all parts of the world in gas and coke oven plants. After the gas leaves the collecting main it is drawn through tubular condensers, where it is cooled down to the desired temperature. The exhauster then forces the gas through a tar extractor where the last traces of the tar are removed. The gas leaving the tar extractor is naturally saturated with water vapor. After leaving the tar extractor, it passes through a reheater where the temperature of the gas is raised about 15° C. and is no longer saturated for that temperature. It next passes through saturators, containing a saturated solution of ammonuim sulphate and about 5 per cent of sulphuric acid. All the ammonia in the gas is combined with the sulphuric acid in the saturators forming ammonium sulphate, which precipitates out instantly. The salt crystals are removed from the saturator by means of an ejector which discharges into a draining table, and pass from there to centrifuga' driers, then to the storage pile. This process works continuously and *all* the ammonia in the gas is recovered. After the gas leaves the saturators it may be used for any purpose. If used as illuminating gas it must pass through the purifier and from there to the gas holder from which it is distributed to consumers for household and heating purposes. The sulphate received from this process is perfectly white and contains at least 25 per cent of ammonia and only 0.1 to 0.2 per cent of free sulphuric acid. The condensates received from the coolers are collected and the small amount of ammonia water distilled in a still passing the ammonia vapors back into the gas again so that they finally reach the saturators. This direct process is already installed in a great many plants and works with great success. The advantages over the wash processes are:

1. Smaller amount of labor required.
2. Less floor space.

3. No water for washing is necessary.
4. No pumps for wash water.
5. Less steam consumption by the stills.
6. More complete recovery of ammonia.
7. Can be installed in any climate because it is independent of the temperature of water supply.

The application of coal gases, with which we are all more or less familiar, is in cooking and lighting. We have already explained that with the proper coal, and with the distillation taking place under the proper conditions, the requirements regarding candle power can be easily met. This statement is borne out by the fact that millions of feet of gas for household uses are now produced from chamber ovens and delivered to the consumers in the same condition as it leaves the purifiers.



"C." Koppers Cross Regenerative Combination Oven.

Among the industrial applications of by-product coke oven gases, we wish to take up its use as fuel for boilers, gas engines, open hearth furnaces, heating furnaces, its various uses in foundries, etc.

By-product coke oven gas has an average heating value of 450 to 550 B.t.u. per cu. ft. Its comparison with other fuels will be based on a heating value of 500 B.t.u. We shall also assume a coal of 12,000 B.t.u. and fuel oil of 18,000 B.t.u. per pound as a basis of comparison.

By-product coke oven gas has proved its value as fuel for open hearth furnaces only in the last five or six years. It is now considered as one of the best fuels for this purpose on account of the higher temperature obtainable, a better economy both in the use of heat and in the construction of the furnace, an increased tonnage and lower operating costs as compared with producer gas.

The gas was first used in the same manner as producer gas, being passed through regenerators before meeting with the preheated air in the combustion chamber. This was found unnecessary, as its high heating value enabled sufficiently high temperatures to be maintained without preheating, besides, the gas actually loses approximately 9 per cent of its heating value by preheating. Therefore, the gas is now introduced cold and only the air passed through the regenerators, which allows of smaller regenerators and thus cheaper furnace construction.

On account of the high heating value of this gas a temperature may be maintained considerably higher than with producer gas, allowing a greater tonnage for the furnace. The output in some cases has been known to increase 15 to 20 per cent. Also by using the fuel which is already a gas, operating costs will be reduced by the amount of the operating costs of the producers. It has been claimed by some that the life of the furnace was shortened by the higher temperatures obtained with this gas, also, that the light gas had a tendency to rise and burn along the top of the furnace instead of just over the bath. These difficulties are being rapidly overcome and cases have been cited where the roof has actually stood more heats than with producer gas before repairing was necessary, while the life of the checkers was greatly increased. This is due more perhaps to the more skillful handling of the furnace as the workmen become better acquainted with the peculiarities of the gas.

Blast furnace gas is too low in heating value for use as an open hearth fuel, but when mixed with coke oven gas in the ratio of 3 or 4 to 1 volume of coke oven gas, sufficiently high temperatures have been maintained.

The gas required per ton of open hearth product will vary with the size of the furnace and the nature of the charge. For a liberal estimate let us take the results reported from a 4-ton open hearth furnace design for producer gas but now using coke oven gas. In this furnace 880 pounds of coal per ton of product were replaced by 15,400 cu. ft. of coke oven gas per ton, making the gas equivalent of a net ton of coal as open hearth fuel, 35,000 cu. ft.

Next to its use as open hearth fuel, coke oven gas is probably best adapted to heating furnaces. Here again the operating cost is reduced and the tonnage of the furnaces greatly increased. The gas required per ton of product varies greatly according to the size of the material to be heated, ranging from 1,500 cu. ft. per ton in large ingot heating furnaces to 33,000 cu. ft. per ton of smaller material, such as bolt and nut rods. Part of this great difference is due also to the ingots being charged directly from the stripper while

the small rods are charged cold. In this capacity the gas equivalent of a net ton of coal will average approximately 29,000 cu. ft.

As a boiler fuel, coke oven gas has proved economical for replacing coal. The lower repair and labor costs for gas-fired boilers are just as great a saving as where producers are replaced by coke oven gas. The efficiency of the boiler is also increased approximately 10 per cent. Under a boiler approximately 100 cu. ft. of gas are required per boiler horse power, or the gas equivalent of one net ton of coal as boiler fuel is 35,400 cu. ft.

Since we have no reliable information at present for a comparison of coke oven gas with fuel oil, if we assume that the two fuels are used with the same efficiency, we find the gas equivalent of 1 gallon of oil to be 264 cu. ft.

In the foundry, the coke oven gas adapts itself to various uses, all of which tend to make the work of the foundry lighter and more pleasant and to decrease the cost of the products. In many foundries, where it is available, it has replaced coal and coke as fuel in every use except the cupolas and even there it is often used for kindling. It lends itself very readily to drying molds and ladles, and to firing coke ovens. To these foundry applications already mentioned, must be added the furnaces for melting brass and other alloys as well as pits for crucible heating.

Last, but not least, of the industrial applications of coke oven gas is in the gas engine. It has not, as yet come into general use in gas engines, owing principally to the effect of the sulphur and cyanogen compounds upon the piston, the interior of the cylinder, and the valves. These difficulties are overcome by purifying the gas and with rapid improvement in design, there is no doubt but coke oven gas engines will come into common use. Much of the progress in the development of these engines has been made in Germany, where there are many power plants now using by-product coke oven gas in gas engines. One of the most interesting ones of these is described by C. A. Tupper, in *Mining and Engineering World* for Dec. 23, 1911. This plant was located in Rhenish, Prussia, and consisted of two electrical generator stations operated in parallel, one equipped with steam turbines and the other with gas engines operated on by-product coke oven gas. Power was developed by the gas engine with 30 cu. ft. of 500 B.t.u. gas per kw. hr., by the steam turbine with 13.6 pounds of steam per kw. hour. This amount of steam would require in the neighborhood of 40 cu. ft. of gas to develop it in steam boilers, to say nothing of losses in steam lines and condenser auxiliaries.

Let us see what we may do with a ton of coal. First we may coke it in a bee-hive oven and get in return 65 per cent or 1,300 lbs. of coke with which we may produce something less than 1,200 pounds of pig iron.

Again, let us put it in a by-product coke oven. We get in return 1,500 lbs. of coke which will produce over 1,350 lbs. of pig iron, about 17c. worth of tar, 60c. (net) worth of ammonium sulphate and still have sufficient surplus gas to replace 286 pounds of coal in the open hearth furnace or under boilers, or produce 224 electrical horse power. In other words, our saving by the by-product ovens over the bee-hive is 200 lbs. of coke, 77c. worth of tar and ammonia and 224 electrical horse power.

As mentioned before, it is very important to have the best possible heat distribution on the oven in order to get the most by-products in the gas as well as the best coke, and we wish to explain to you a coke oven which has all the features required to obtain this even distribution of the heat. This is the Koppers Regenerative Coke and Gas Oven.

A battery of Koppers regenerative coke ovens (Fig. 1) consists of a series of oven chambers placed side by side. The wall between two ovens serves as a heating wall. This heating wall consists of about 28 to 30 vertical flues in which the combustion takes place. Underneath these vertical flues is a gas distributing flue. Every vertical flue is connected to this gas flue by a gas nozzle through which the gas is introduced into the vertical flues for combustion. These nozzles are interchangeable, so that a nozzle with any desired size of opening can be used. Directly underneath each oven chamber is a regenerator where the air used for combustion in the vertical flues is preheated. It enters the regenerators at the bottom and passes up through the hot checker work and then to each individual flue, where the combustion of the gas takes place. The amount of air admitted to the regenerator can be regulated by means of individual dampers for each oven. During one period the gas burns in one-half of the vertical flues of the oven walls and the products of combustion pass into a horizontal flue which is placed just above the vertical flues and from there to the other half of the vertical flues of the oven walls, then down to the regenerator on the other side where it gives off its heat to the checker brick and passes into a common flue leading to the chimney. The draft in each regenerator can be regulated by means of a damper at the entrance to the regenerators and in each vertical flue by sliding bricks which are placed at the outlet of each vertical flue just where they connect to the horizontal flue. With these sliding bricks, the combustion in each vertical flue as well as the length of the flame and the draft in each individual flue can be regulated. The setting of these sliding bricks can be regulated through openings from the top of the battery which means that each individual flue can be easily inspected. After the gas is burned on one side for a period of one-half an hour, this process is reversed and the gas is burned in the vertical flues through which the waste gases passed before reversing.

Reversing of gas and air is done automatically by means of cables which are connected to the covers of

the individual flue boxes on each regenerator as well as to the gas cocks in the connections leading to the gas distributing flue underneath the vertical flues.

It is easily seen that with this design of oven absolutely uniform heats can be maintained over the entire oven wall, for the operator is able to inspect every part of the oven wall and regulate the combustion accordingly. The amount of gas used to coke a coal in these ovens amounts to but 45 or 50 per cent of the gas produced, a figure which is not reached by any other coke oven construction. The remaining 50 to 55 per cent of the gas produced from these ovens is received in form of gas and not in form of waste heat, as is the case in some other oven designs where the waste heat is used for raising steam in boilers. By using waste heat for raising steam, the utilization of the B.t.u. is not as economical as when surplus gas is burned under a boiler. By using surplus gas in a boiler, one is able to regulate the amount of gas and air so as to obtain the most efficient and economic operation of the boilers. The temperature of the waste gases after they leave the regenerators on the Koppers ovens is so low that they can be discharged directly through the chimney. The advantage of the regenerators over the recuperators is well known.

In gas plants, where the main product is illuminating gas, and where there is no market for coke, the H. Koppers Co. has constructed a gas oven (Fig. 2) which is similar to the coke oven. Instead of using half of the gas as fuel, all the gas made can be used as illuminating gas, the oven being heated with producer gas. Coke breeze and small coke from the ovens can be utilized as fuel for the producers. The regenerators on the gas ovens are divided into two parts by means of a vertical wall which extends the entire length of the oven chamber and no gas distributing flue connected to the vertical flues is used. The producer gas as well as the air necessary for combustion is preheated in these regenerators and meets in the vertical flues where combustion takes place. The amount of underfiring, that is, the amount of fuel used in the producers in order to gasify the coal in the oven chambers, is much less than that used for gasifying coal in retorts. The amount of underfiring in retorts is 16 to 20 per cent, whereas in Koppers gas ovens it amounts to 10 to 12 per cent. The underfiring, of course, depends to some extent on the kind and efficiencies of the producers installed.

The Koppers Co. has also constructed a combination oven (Fig. 3) which can be used either as a coke oven heated with gas produced in the ovens, or as a gas oven heated with gas generated in gas producers. This oven is similar to the gas oven just described with the addition of the gas distributing flue underneath the vertical flues as on coke ovens. When operating on producer gas, the gas is sent through half the regenerators before entering the vertical flues, which allows the use of all the gas produced in the ovens for illuminating gas. If only half the amount of illuminating gas is desired, this oven can be heated with a separated fuel gas, passing this fuel gas to the gas distributing flue, the air being preheated in all the regenerators. This oven is one of the most flexible ovens ever constructed. A plant having these combination ovens can be first operated as a coke plant by separating half of the gas and using the other half as fuel gas. The plant can be built large enough to operate on a long coking time and with the increase of illuminating gas consumption the coking time can be lowered gradually so as to produce more gas corresponding to the amount of illuminating gas desired. After the limit of the coking time is reached, then gas producers can be installed and the oven heated with producer gas made from coke breeze. This allows all the gas made in the oven to be used as illuminating gas, and the coking time can be increased again. With the increasing demand for illuminating gas the coking time can be then decreased until the limit of coking time is again reached. A further increase on the demand of illuminating gas naturally would mean building additional ovens.

The government of Brazil has entered into a contract with an American rubber company to construct a rubber factory at Rio de Janeiro, Brazil. The terms of this contract as published by the government and translation thereof can be obtained from the Bureau of Foreign Domestic Commerce, Washington, D. C. Under the terms of this contract the company's initial capital of $3,000,000 is to be employed in installing and exploiting this factory, which is to be inaugurated by April 9, 1914. The factory and its products are to be regularly inspected by the government; the factory to revert to the government after 90 years. The following favors are granted this company: A premium in cash corresponding to one-fourth of the expense of the first establishment, but not to exceed Rs. 500,000,000 (about $160,000); free entry on all materials, machinery, etc., for the factory; right of disappropriation for public utility; preference given by the government for buying its products used in the army and navy.

A new German law, dated March 31, 1913, makes certain alterations in the law for patents and trademarks. Citizens of the German empire may now claim the benefit of the laws for the protection of utility models and trade-marks and the law of unfair competition even though they do not have a residence or establishment in Germany. A feature of the new law is the section dealing with association trade-marks. These are distinguishing marks registered by associations of manufacturers or merchants for exclusive use in connection with the goods of members of the association. They are said to be of considerable importance in Austria-Hungary and some other countries. Heretofore there has been no provision for them in the German laws.

METALLURGY.

METHOD FOR THE RAPID DETERMINATION OF TOTAL CARBON IN IRON, STEEL, CAST-IRON AND IN THE IRON ALLOYS.*

By H. DE NOLLY,†

The object aimed at was to arrive at a sufficiently accurate method for determining the proportion of carbon, which might replace those now followed in the laboratories, and be at the same time sufficiently rapid to allow the following up of a heat, in the Siemens-Martin or in the electric furnace. The method, described below, has all the advantages of the dry method and, from the point of view of rapidity, is superior to the Eggertz colorimetric process.

PRINCIPLE.

The method consists in burning the metal in a limited volume of pure oxygen, by starting ignition electrically, in causing the carbonic acid resulting from the oxidizing of the carbon to be absorbed in a known quantity of alkaline solution placed in the flask itself in which combustion takes place, and in determining the excess of free alkali by means of a titrated sulphuric acid liquor, in the presence of phenolphtaleine as an indicator.

The two following equations show the reactions:

$$\begin{cases} 4\ (Na\ OH) + 2\ Co_2 = 2\ (Na_2\ Co_3) + 2\ (H_2\ O) \\ 2\ (Na_2\ CO_3) + So_4\ H_2 = 2\ NaHCO_3 + Na_2\ SO_4) \end{cases}$$

REAGENTS REQUIRED.

I.—Absorbing liquor:
- NaOH = 4 grammes
- Water = 1000 c. c.

II.—Indicator:
- Phenol-phtaleine = 1 gramme
- Alcohol at 90° = 100 c. c.

III.—Titrated sulphuric acid solution:
- $SO_4\ H_2$ = 4.083 grammes
- Water = sufficient quantity to make up to one litre.

This liquor contains 3.333 grammes of SO_3 per litre and one cubic centimetre corresponds to 1 milligramme of C. The SO_3 is exactly determined as $BaSO_4$ by means of $BaCl_2$.

DESCRIPTION OF THE APPARATUS.

The apparatus consists mainly of the following:

1.—A conical or cylindrical flask of about one litre capacity, of Jena glass, having a wide neck closed by an indiarubber stopper made with three openings: through these run two copper rods, fitted with ignition electrodes, and a tube, also of copper, which serves to supply the oxygen required for combustion to the top of an asbestos cup which contains the metal for analysis. The cup is carried by a bent copper rod fitted to the oxygen supply tube, by means of a slide provided with a thumb-screw, which allows regulation for height.

2.—A receiver containing oxygen under a pressure of 30 to 40 cm. of water, which serves to maintain a practically constant pressure and a high oxidizing atmosphere in the combustion flask, by renewing the oxygen supply according as it is being utilized in the reaction. The water in the receiver contains a little potash for removing from the oxygen all traces of carbonic acid which it might contain.

3.—A small bottle is inserted between the oxygen receiver and the conical flask, being connected to both by india rubber tubes. This small bottle acts as a seal; it contains a small quantity of mercury through which the oxygen is made to flow, by means of a plunger tube, in passing from one to the other. This arrangement prevents gas from being driven back into the oxygen receiver, should a too active combustion produce an excess of pressure in the conical flask.

The cups which serve to contain the metal for combustion, and have to be changed for each separate operation, are very cheaply made, by dishing circular pieces 50 m. m. (2 inches) in diameter cut out of asbestos-board 1 to 2 mm. (0.039 to 0.78 m.) thick. The dishing is very easily accomplished, by driving the circular pieces, slightly damped, in a steel ring 30 mm. (1.180 in.) inside diameter, using a brass mandrel 25 mm. (0.984 in.) in outside diameter. The cups then undergo heating for several hours at a high temperature, in a muffle furnace in order to destroy all organic matter and to decompose the carbonates which might be found in the asbestos.

DESCRIPTION OF THE OPERATION.

About 1 or 2 grammes of the metal to be analyzed is placed in the asbestos cup, fine drillings of the metal being used. Should the metal be in a powdered state, or in the form of large turnings, it should be mixed with 0.100 or 0.200 grammes of PbO_2 or Bi_2O_4, in order to facilitate combustion; combustion would risk being incomplete were this precaution not taken.

The cup containing the metal is placed on its support, its position being adjusted by means of the slide and thumb-screw in such a way that its rim is at a distance of from 5 to 6 mm. (0.196 to 0.236 in.) from the opening of the tube supplying the oxygen, the points of the electrodes touching the metal turnings. The whole is then placed, in the conical flask, which has previously been filled with oxygen, or a beaker containing water in which 40 to 50 cubic centimeters of soda solution have been poured.[1] The apparatus is

*Paper presented at 6th Congress of International Association for Testing Materials.

†Compagnie des Forges et Aciéries de la Marine et d'Homécourt, St. Chamond.

[1]When the percentages of carbon are high, it is advisable to double the quantity of soda solution, in order to always have a great excess of free alkali after the absorption of Co^2.

carefully made tight, special care being also taken not to let any of the metal for analysis fall out of the cup; the tap regulating the oxygen supply is opened in order to establish the pressure in the combustion apparatus and an arc is produced between the two electrodes by a double-pole switch, the current intensity

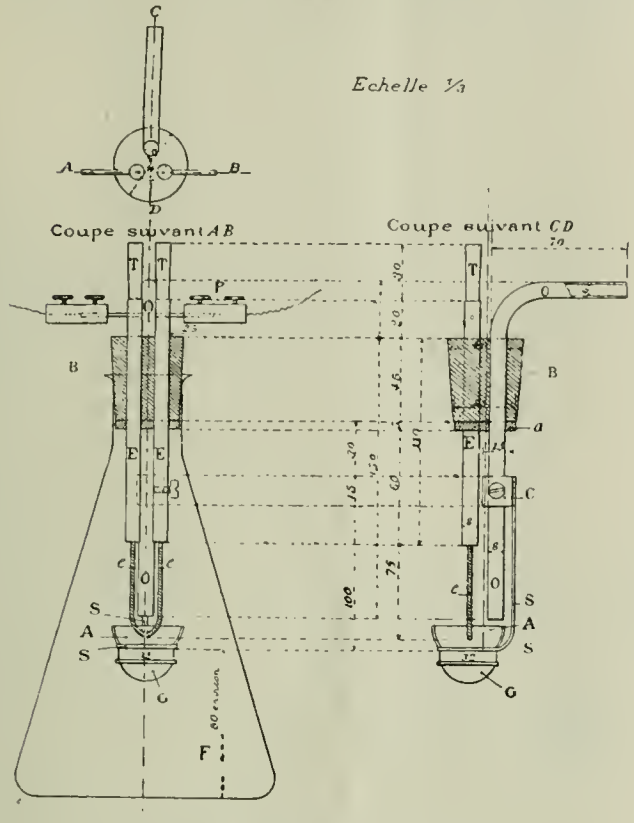


Fig. 1.—Diagram of Apparatus.

(F) Conical-litre flask. (B) India rubber stopper. (a) Asbestos ring protecting the stopper. (E) Electrode carriers. (e) Electrodes. (T) Insulating fibre extensions, for varying the distance between the electrodes. (P) Current collecting rods. (O) Copper pipe for oxygen supply. (C) Slide with screw for regulating height of asbestos cup. (S) Asbestos cup holder. (G) Basket of copper netting or clay cup to contain the oxide which otherwise would fall at the bottom of the flask, when the ashestos cup became damaged.

being limited, by means of a suitable resistance, to 12 or 15 amperes, when the electrodes are short-circuited.

As soon as combustion has started, current is cut-off and the metal generally continues burning. Should combustion cease, or proceed with difficulty, fresh sparks are created by working the switch and by causing the distance between the electrodes to vary by acting on the end pieces; the latter are made of insulating fiber and form the extensions above the india rubber stopper of the current connecting bars. If, on the contrary, reaction is too violent, it can be moderated by stopping the supply of oxygen.

When combustion is complete, the oxygen tap is turned off, the conical flask is cooled by plunging it into water, it is then quickly closed by a solid stopper after removal of the lighting device; it is shaken for 5 to 10 seconds to complete the absorption of the CO^2, the alkaline liquor is poured into a glass and the excess of non-carbonated soda is determined by pouring the titrated sulphuric acid liquor into a beaker graduated in 1/10 cubic centimetres until the pink tint due to the phenolphtaleine disappears.

The ratio between the two solutions, alkaline and sulphuric, is established and from the difference between the two titrations the proportion of carbon is arrived at, bearing in mind that if the sulphuric acid standard liquor contains exactly 3.333 grammes of SO^3 per litre, 1 cubic centimetre of this solution corresponds to 1 milligramme of carbon.

It will be noted that by proceeding thus no account need be taken of the slight carbonating—which is almost inevitable—of the reserve of absorbing solution.

The process enables the carrying out of a determination for carbon in 5 to 7 minutes, equal in precision to that obtained with the Wiborg apparatus. It is applicable to all kinds of steel, the presence of chromium, nickel, tungsten, molybdenum, vanadium, titanium, etc., leading to no risk of error.

The author has succeeded in applying the method to cast iron tests and to all iron alloys, by basing his researches upon the following observations:

1. When the proportions of carbon are too low, the metal burns incompletely but in no case is there any carbon monoxide produced.

2. Combustion is all the more incomplete the higher the proportion of carbon; an occurrence takes place similar to that which obtains in the cutting of metals by means of the oxygen blow-pipe, when the operation becomes gradually difficult as the proportion of carbon in the metal increases, the operation being impossible in the case of cast iron, which melts without burning.

The remedy consisted in placing the too highly

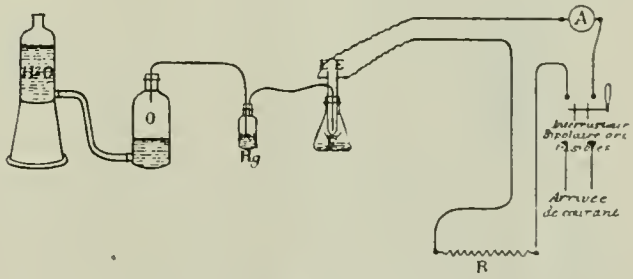


Fig. 2.—Diagram Showing Arrangement of Apparatus.

(H^2O) Bottle giving the pressure. (O) Bottle containing the oxygen. (Hg) Mercury seal. (A) Ammeter. (R) Resistance designed for a 12 to 15 ampere current when the electrodes are short-circuited. (r) Tap.

carburized metal in a larger quantity of iron or extra-mild steel; this has given perfectly good results, the addition of an oxidizing body, lead bioxide, or bismuth tetraoxide, also facilitating the integral combustion.

The following list gives the weights of material to be used in order to obtain exact determinations of carbon in the case of cast iron and the various ferro-alloys:

For all cast-irons	0.500 gr. cast-iron+0.200 gr. PbO^2+1 gr. extra-mild steel.
For ferro-chrome with 6 to 10% C.	0.250 gr. ferro+0.200 gr. PbO^2+2 gr. extra-mild steel.
For ferro-	

chrome with 1 to 5% C.	0.500 gr. ferro+0.200 gr. PbO^2+1 gr. extra-mild steel.
For ferro manganese	0.250 gr. ferro+0.200 gr. PbO^2+1 gr. extra-mild steel.
	0.500 gr. ferro+0.200 gr. PbO^2+2 gr. extra-mild steel.
For ferro-silicon with 10 to 90% Si	0.500 gr. ferro+0.200 gr. PbO^2+1 gr. extra-mild steel.
For ferro-Mo	0.500 gr. ferro+0.500 gr.[2]) PbO^2+1 gr. extra-mild steel.
For ferro-Tu	0.500 gr. ferro+0.100 gr.[3] PbO^2+1 gr. extra-mild steel.

The very fine turnings of extra-mild steel—these are made as fine as practicable—are placed at the bottom of the asbestos cup and the mixture of pulverized cast iron or ferro-alloys is uniformly spread over it with the powdered lead-oxide.

The pulverized cast iron is passed through an 80-mesh screen and the ferro-alloys through a 120-mesh screen.

In this manner even grey cast iron containing a large percentage of graphite is burnt completely.

Correction is made by effecting a blank test in like conditions with all the reagents, and without the metal requiring analysis; steel should be selected as low in carbon and as pure as possible (C = 0.050 to 0.080).

NOTE.

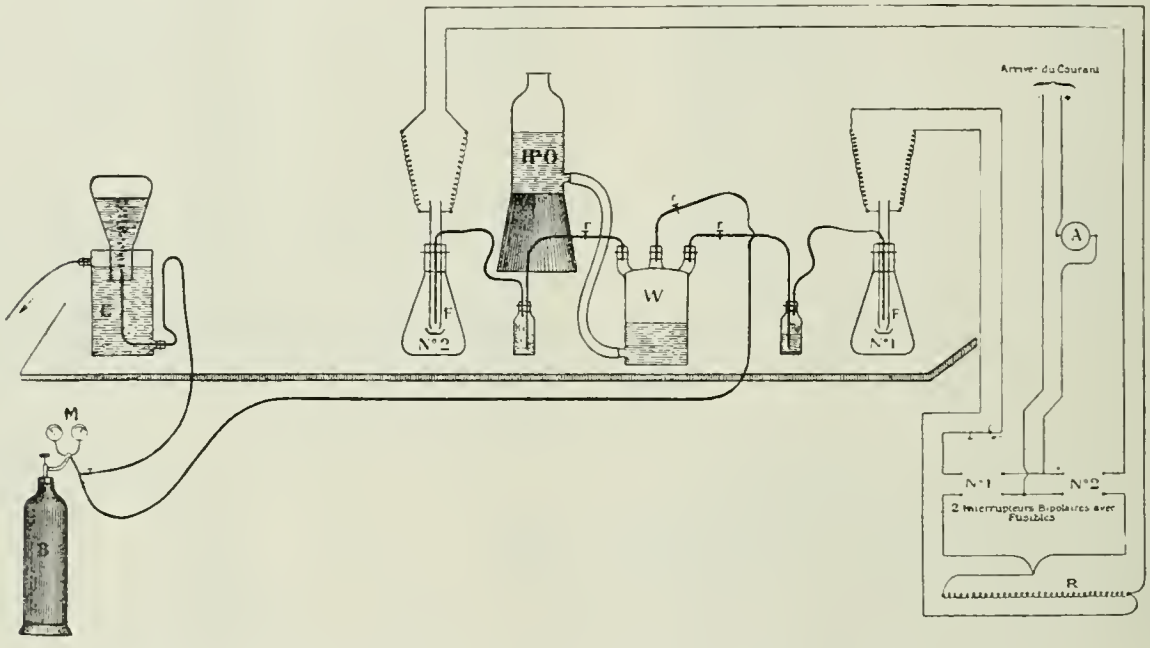
I. When powdered hardened steels are dealt with, it is necessary in order to effect a good combustion, to pass the powder through a 100-mesh screen and to add 0.200 to 0.300 of PbO^2 per gramme of steel, this facilitating reaction by dividing up the material.

II. In the case of steels containing over 1.5 per cent of carbon, it is necessary to have large and thin drillings obtained by drilling at high speed with a good drill. Needle shaped drillings, dust and thick shavings should not be taken, or, if taken, a combustible material should be added.

For determining the proportions exceeding 1.5 per cent of carbon it is advisable to dilute the liquor to 500 cubic centimetre in order that the disappearing of the tint be quickly discernible, and it is prudent to return to the soda solution until the reappearance of the pink tint.

III. Numerous tests have shown that S has no influence or, it should rather be said, has but a very slightly appreciable influence, even in the case of metals containing as much as 0.800 per cent of S. In determining the sulphur by means of bariumchloride in the soda liquor rendered hydrochloric, the author found only traces of bariumsulphate. The figures for the carbon were perfectly accurate and required no correction. The sulphate resulting from the oxidizing should all remain in the cup whence it can be taken for purposes of determination.

IV. The same applies to phosphorus, which all remains in the cup as phosphate. Even by operating with cast iron containing 2 per cent of P the C determinations have remained accurate and no trace of the P could be found in the soda liquor.



Arrangement of Apparatus for Double Installation for Rapid Determination of Carbon.

(B) Oxygen bottle. (M) Pressure gauge and regulator. (C) Beaker for filling flasks with oxygen. (W) Woolf bottle supplying oxygen to the conical flasks. (H^2O) Bottle giving the pressure. (Hg) Mercury seals. (A) Ammeter. (r) Tap. (R) Resistance designed for a 12 to 15 ampere current when the electrodes are shortcircuited. (F) Combustion flasks.

The production of raw iron in Germany, about one-fifth of which is mined in Alsace-Lorraine, amounted to 16,280,000 tons in the first 11 months of 1912 and 14,160,000 tons in the same period of 1911.

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[2]When less PbO^2 is used there occurs a volatilisation of a small proportion of molybdic acid which passes into the soda liquor and impairs titration.

[3]With 0.200 PbO^2, combustion is too violent and the asbestos cup becomes damaged.

THE LABORATORY

METHODS OF ANALYSIS USED IN THE LABORATORIES OF THE ARMOUR INSTITUTE OF TECHNOLOGY.

Analysis of Milk and Milk Products.

The methods employed for the analysis of milk and milk products are, in the main, those published and recommended by the United States Department of Agriculture. In the case of some of the determinations, however, it has been found that the desired information may be obtained through simpler and more rapid procedures than those of the official methods.

The following determinations are regularly made: Total solids, ash, fat, casein, lactose, and number of bacteria per cubic centimeter.

The Determination of Total Solids.—A sample of about 5 grams is weighed into a flat aluminum dish and evaporated to constant weight in a water-jacketed air bath heated to boiling temperature. The final weighing must be made very rapidly to avoid absorption of water from the air.

Ash.—About 20 grams of samples are weighed into a tared platinum dish, 6 cc. of nitric acid (sp. gr. 1.42) added, and the whole evaporated to dryness on the water bath. The residue is finally ignited, at the lowest possible temperature in an electrically heated muffle until the carbon is completely burned out, leaving a white ash. The whole is then cooled in a dessicator and weighed.

Total Nitrogenous Matter.—A combination of the official Kjeldahl and Gunning Methods is used, for which the following reagents ar required:

(1) An accurately standardized solution of hydrochloric acid, of about tenth normal strength. This should be standardized by precipitation of the chlorine as silver chloride which is weighed in a Gooch crucible.

(2) A standard alkali solution (NaOH) whose value in terms of the above acid is accurately known. It is convenient to have these solutions exactly equivalent to each other.

In all titrations cochineal is recommended as an indicator. It is prepared as follows: 3 grams pulverized cochineal is extracted for several days, with frequent shakings, with a mixture of 50 cc. alcohol and 200 cc. distilled water, and the whole filtered.

Pure sulphuric acid, sp. gr. 1.84, a saturated solution of NaOH, a solution of potassium sulphide, 40 grams, per litre, powdered potassium sulphate, pure mercury, and some small lumps of pumice stone are also required.

Upon these reagents blank determinations should be made to make sure that all are nitrogen free, or to provide a constant correction.

Procedure.—A 5 gm. sample of milk is placed in the Kjeldahl digestion flask (used also for the distillation) where it is mixed with 10 gms. K_2SO_4 and 0.66 gm. of mercury, and 25 cc. of conc. H_2SO_4 added. The mixture is heated gently until frothing ceases, and then digested at the full heat of the naked bunsen flame until colorless or nearly so, and a short time after that point is reached. This should require less than two hours, a much shorter time than either of the official methods.

When the digestion is complete, the flask and contents are allowed to cool, and the solution diluted to 200 cc., a few pieces of pumice being added to prevent bumping and 25 cc. of K_2S solution to precipitate the mercury. The acid is then neutralized and the ammonia liberated by the addition of 60 cc. of the strong alkali solution, the solution being poured down the side of the inclined flask so that it may not mix with the acid solution. The flask is connected with the block tin condenser by means of a bulb tube to prevent any of the alkali solution from being carried over mechanically, and the end of the delivery tube of the condenser placed under the surface of 40 cc. of the N/10 acid in an Erlenmeyer flask. When all is ready, the distillation flask is rotated to mix the solutions, and heat applied. The whole is boiled briskly until about 150 cc. of distillate has passed over, this being sufficient to assure the elimination of all ammonia. At this point the delivery tube is disconnected, the flask removed and its contents titrated with the standard alkali. The net volume of acid solution times the factor gives net volume of N/10 acid which is equal to the vol. of N/10 NH_3 and of N/10 nitrogen which has a strength of 1 cc.= 0.0014 gm.,

$$\text{so} \quad \frac{\text{cc. N/10 acid used} \times 0.0014}{\text{Wt. sample}} \times 100 = \%\ \text{N}$$

% nitrogen × 6.38 = % nitrogenous compounds.

It is frequently desirable to determine pure casein as well as total nitrogenous substances. Casein may be determined in the following way:

(1) A sample of 10 grams of the fresh milk is made up to 100 cc. with water at 40° to 42° C. in a beaker. To this is added at once 1.5 cc. of a 10 per cent solution of acetic acid. The solution is stirred and allowed to stand for from three to five minutes, when it is decanted through a filter, the precipitate washed several times by decantation, using cold water, and finally transferred to the filter and the washing completed. The precipitated casein may run

through the filter at first. In this case, the filtrate should be returned to the filter until it is perfectly clear. The precipitate obtained is run for nitrogen by the method described for total nitrogen.

Per cent nitrogen $\times$ 6.38 = per cent casein.

The difference between the total nitrogenous material and the casein is approximately equal to the albumen.

Fat.—For this determination two methods are given:

(1) The Babcock method.

(2) A gravimetric method.

(1) The Babcock fat test requires a special apparatus consisting of a centrifuge capable of about 1,000 revolutions per minute, and properly graduated bottles and pipettes.

A sample of 17.6 cc. of the thoroughly mixed sample of milk is pipetted into the test bottle and 17.6 cc. of commercial H_2SO_4 (sp. gr. 1.82-18.3) added. After mixing the solution is whirled in the centrifuge for four minutes. Hot water is added up to the neck of the bottle and the bottle whirled for one minute, and finally boiling water again added until the layer of fat comes within the scale, and the whole again for one minute. The readings on the scale give per cent of fat direct.

(2) The gravimetric method for fat is carried out as follows:

A paper coil is prepared by rolling strips of thick filter paper 2.5 by 25 inches, into solid rolls. Such proper coils may also be purchased prepared for use. They should be thoroughly extracted with ether before use.

About 6-8 grams of milk is weighed in a weighing bottle, and about 5 cc. of this absorbed into the paper coil, care being taken to keep one end of the same dry. A second weighing of the bottle and the milk remaining gives the weight of the sample, which should be about 5 grams. The sample is dried thoroughly in a water-jacketed air bath, and is then extracted in a Soxhlet or similar type of extraction apparatus for several hours with petroleum ether. After 6 hours the ether is evaporated off and the fat weighed.

Lactose.—The determination of lactose or milk sugar is most conveniently made by means of the polariscope such as is used in sugar analysis, and which reads percentage of cane sugar direct. Lacking such an instrument, the gravimetric method is satisfactory, though somewhat longer.

(1) Optical method: For this a sugar polariscope or Sacharimeter is employed, whose normal weight for sucrose is 26.048 grams.

By using a constant, exact weight of sample based upon the specific rotary power of pure lactose, it is possible to make the polariscope read percentage direct.

To get the exact weight, it is best to determine the specific gravity of the milk, either by the Westphal balance or by a delicate hydrometer, and then measuring accurately the volume corresponding to the sp. gr. in the appended table:

Table for instrument whose normal weight for sucrose is 26.048 grams:

Sp. gr.	Volume of milk c. c.
1.024	64.30
1.026	64.40
1.028	64.15
1.030	64.00
1.032	63.90
1.034	63.8
1.035	63.7

The volume indicated from the table is run into the flask that corresponds to the instrument in its graduation, and to it is added 30 cc. of a mercuric iodide solution (33.2 gm. KI, 13.5 grams $HgCl_2$, and 20 cc. glacial acetic acid dissolved in 640 cc. of water), the whole made up to the mark of the flask and mixed thoroughly. It is then filtered through a dry filter, a portion put into the polariscope tube and the readings made.

100 m. m. tube reads percent direct.
200 m. m. tube reading is divided by 2.
400 m. m. tube reading is divided by 4.

(2) Gravimetric Method.—This depends upon the reducing action of lactose upon alkaline copper tartrate solutions the weight of Cu_2O formed being a function of the weight of lactose present. Tables of weights of sugars corresponding to given weights of Cu_2O may be found in any of the works upon sugar analysis, food analysis, and kindred subjects.

The solutions used is Soxhlet's modification of Fehling's solution, made as follows:

(1) $CuSO_4 . 5H_2O$, 34.639 grams dissolved in water and made up to 500 cc.

(2) $KNaC_4H_4O_6$ (Rochelle salts), 173 grams and sodium hydroxide 50 grams made up to 500 cc.

These solutions are mixed volume for volume just before use.

(3) A half normal solution of NaOH.

25 cc. of milk are diluted with 400 cc. of water, 10 cc. of above described copper sulphate solution and 8.8 cc. of the half normal sodium hydroxide solution added. The mixture must be acid at the point and still contain copper in solution. The whole is then diluted to exactly 500 cc., mixed thoroughly and filtered through a dry paper.

Lactose is now determined upon alliquot parts of this solution as follows:

50 cc. of the mixed copper reagent (half and half of copper sulphate and Rochelle salts solutions) are heated to boiling, 100 cc. of the prepared sugar solution added, and the whole boiled for six minutes. The red precipitate of Cu_2O is thrown on a tared Gooch crucible, washed with hot water, then with alcohol, finally with ether, and dried to constant weight at 100° C. Weight $Cu_2O \times 0.8883$ = weight Cu.

From the weight in milligrams of Cu, the corresponding weight of lactose is taken from the table, which may be found in any work upon commercial

organic analysis, food analysis, or from Bul. 107 U. S. Department of Agriculture.

$$\frac{25 \text{ cc.} \times \text{sp. gr.}}{5} = \text{weight sample of milk.}$$

$$\frac{\text{wt. of lactose (from table)}}{\text{wt. sample}} \times 100 = \%\ \text{lactose.}$$

Bacterial Count.—No milk analysis is complete without a count of the bacteria. For this purpose one cc. of the sample is measured into a sterile flask with a sterile pipette, and diluted to 500 cc. with sterile water. One cc. of this solution is taken in a fresh pipette and again diluted to 100 cc.

Six tubes of nutrient agar are placed in hot water, the agar melted, and then allowed to cool to 40° C.

One cc. of the low dilution is placed in each of three sterile Petri dishes, properly marked. Three samples of the high dilution are similarly prepared. The agar from the tubes is then poured into the dishes, care being taken to allow as little exposure to the air as possible, and the solution and agar mixed by gently flowing the contents of the dish back and forth. The agar is allowed to set and the dishes are then inverted and incubated at a temperature of 38° C. for 24 hours, when the number of colonies is counted in each.

Average of counts for the first dilution multiplied by 500, gives bacteria per cc. of the original milk, and for the second dilution, the number of colonies is multiplied by 50,000.

A U. S. Consular Report states that the income of the Nobel Dynamite Trust Co. for the year ended April 30 was the same as for the previous year. Expenses were slightly lower so that the net profit came out at $1,852,800, against $1,825,600 in 1910-11. With $16,800 brought forward, this admits of 5 per cent on the preference shares, 10 per cent (including 2 per cent bonus) on the ordinary shares, placing $500,000 to reserve—making it $3,500,000—and carrying forward $27,400. Considering the size of the share capital, of which $11,123,000 has been issued and paid up, it is commented in England that the equability of the dividends is clear proof of the consistency of the business. The following record of the trust's dividends speaks for itself: 1901-2, 9 per cent; 1902-3, 7½ per cent; 1903-4, 8 per cent, and for each of the nine years to 1912-13, 10 per cent. A considerable proportion of the profit is doubtless earned by Nobel's Explosives Co. of Glasgow, the authorized capital of which is $5,000,000, of which $4,000,000 is held by or on behalf of the Nobel dynamite trust.

In the first 11 months of 1912, 162,000,000 tons of coal were mined in Germany, against 137,000,000 tons in the same period of 1911. Alsace-Lorraine participated in this production to the extent of some 3,000,000 tons.

PROPOSAL FOR ESTABLISHING A STANDARD SO_3 CONTENT FOR PORTLAND CEMENT.*

BY THE VEREIN DEUTSCHER PORTLANDZEMENT-FABRIKATEN, KALKBERGE.

Portland cement is known to contain small quantities of sulphatic salts, originating partly in the raw materials and coal, and partly added, in the form of crude gypsum (hydrated calcium sulphate), in the process of grinding the calcined cement, for the purpose of controlling the time of setting. The total content of sulphates in a cement is generally stated in terms of sulphur trioxide (SO_3).

These small quantities of sulphur trioxide occurring in normal Portland cement, are quite uninjurious to its practical application; and it is only when the amount exceeds a certain limit that, during storage under water, a supplementary expansion—which may sometimes be dangerous—occurs in the hardened cement, owing to the formation of calcium-aluminium sulphate. This substance is also formed when the amount of SO_3 is small, but in such event helps to increase the strength of the mass by making it more compact.

When the Standard Specifications of Quality and Testing of Portland Cement were redrafted in Germany, the maximum permissible limit of SO_3 was fixed at 2.5 per cent on the basis of extensive experiments.

In other countries the following maximum limits are in force:

England	2.75% SO_3
Austria	2.50% SO_3
Canada	2.0 % SO_3
United States	1.75% SO_3
Russia	1.75% SO_3

In the countries named below, the limit differs, according as the cement is to be used in fresh or salt water:

	Fresh water.	Salt water.
France	3.0%	1.5% SO_3
Brazil	3.0%	1.5% SO_3
Japan	2.0%	1.5% SO_3
Argentina	2.4%	1.2% SO_3

There is, however, no reason why the amount of SO_3, prescribed for fresh water should act differently when the cement is hardened in salt water. In hardening in fresh water, an amount of SO_3 slightly exceeding 2 per cent produces a very small degree of expansion by the formation of calcium-aluminium sulphate; and the same process occurs when the hardening takes place in salt water. This minute expansion cannot have any injurious results. If, however, the sea water (containing magnesium sulphate) is able to penetrate into the cement mass permanently—which happens principally in the case of cement that is not compact—the result is that the cement is attacked. In the opinion of various investigators, the

*Paper presented at the 6th Congress, International Association for Testing Materials.

magnesium sulphate of the sea water combines with the lime in the cement to form calcium sulphate and magnesium hydroxide. This latter is deposited in the pores of the cement, whereas the calcium sulphate forms calcium-aluminium sulphate with the alumina of the cement, a large quantity of water of crystallization being absorbed. In the event of the action of the sea water being continuous, the considerable expansion resulting from the above named reaction may lead to the destruction of the mass. Hence, it is not the small percentage of SO_3 in the cement which plays a part in the destruction of the mass, but the magnesium sulphate that penetrates continuously from the sea water into the porous cement mortar. This point has been always emphasized by the German Portland Cement Manufacturers' Association; and the late Prof. Dr. W. Michaelis also mentioned it specially at the last general meeting of this association.

We will not now go into other possible causes of the destructive action of sea water, wishing to confine ourselves exclusively to the action of sulphuric acid. We must not, however, omit to mention—as has, moreover, been insisted on frequently and by different authorities—that, in structures exposed to sea water, the mortar used must be as compact as possible, in order to prevent the sea water from penetrating the structure, and to enable the latter more effectually to withstand chemical and mechanical influences.

In order to establish beyond doubt that the percentage of 2.5 per cent of SO_3, as allowed in the German Specification, is quite unobjectionable; and more particularly in view of the fact that the Argentine Specification has recently increased the SO_3 limit from 1.0 per cent to 1.2 per cent in cement for marine structures; the German Portland Cement Manufacturers' Association in 1907 arranged with the Royal Laboratory for Testing Materials, Gross-Lichterfelde, for the performance of tests in this connection, over a period of 10 years, at the island of Sylt in the North Sea.

The materials used consisted of a Portland cement (S), containing 1.19 per cent of SO_3 and employed for all purposes, marine structures included; and another Portland cement (B), which contained only a very small proportion of SO_3 namely 0.57 per cent. Owing to this low percentage, this cement is specially preferred in France for marine structures, e. g., in the harbor at Boulogne, and more particularly in Argentina. It was supplied to the Royal Testing Laboratory by the makers.

Under the standard test after hardening in water for 28 days cement S gave the tensile strength 399 kg per sq. cm. and cement B 169 kg per sq. cm. This low tensile value of cement B is probably due to its coarse grain, the residue on a 5000-mesh sieve amounting to 36 per cent.

The following test pieces were prepared from these two cements, both in their original condition as received, and after the SO_3 content had been raised to 2.5 per cent by suitable additions of crude gypsum:

1. Compression-test cubes (7 cm. side), mixed in the proportions 1:2 and 1:4 with Sylt sand, for hardening in sea water, fresh water and the open air. Length of hardening period: 28 days, 1 year, 5 years and 10 years.

2. Blocks of about ¾ cbm. capacity, composed of a mixture of 1 part cement, 2 of sand and 3 of stone chippings. After being hardened for 6 months in the air, the blocks were let into the quay wall, where they are exposed to the chemical action and full force of the North Sea waves.

3. Plates measuring 50 by 50 by 8 cm., mixed in the proportions 1:2 and 1:4, half of them being hardened for 4 months and the others for 6 months in the air, and then laid in the harbor dam at Munkmarsch, where they are exposed to intensive action on the part of the water and weather in consequence of the semidiurnal ebb and flow.

The results obtained from these experiments up to the present are briefly recapitulated below:

1. In considering the tensile values after hardening for 1 year (Table 1), it appears that these values are lower throughout in sea water than in fresh water and the open air; and that, in spite of its low percentage of SO_3, cement B behaves less favorably than cement S in sea water. In both cases the raising of the SO_3-content to 2.5 per cent by the addition of gypsum, increased the tensile strength, both in fresh water and in sea water with the exception of the mixture 1:4 of cement S. This mixture gave a slightly lower value in sea water; but the accuracy of this determination has yet to be confirmed at a later stage of hardening

The results of the tensile after 1 year's hardening show that the presence of even 2.5 per cent of SO_3 in cement does not have any injurious influence during hardening in sea water.

2. The concrete blocks made from cement B, showed at the end of 1½ year's hardening in sea water (autumn 1909) such an amount of attrition that the fragments of granite were exposed. The blocks from the same cement with the SO_3-content increased to 2.5 per cent, behaved somewhat better. On the other hand, all the blocks made from cement S had remained in perfect condition. This observation was confirmed in general by the second inspection during the following year, which showed that the cement B, which was alleged to be particularly suitable for marine structures, turned out much worse than the cement S with the high SO_3-content.

3. The same conclusion also resulted from the contemporaneous examination of the plates set up in the mole at the harbor of Munkmarsch. The plates mixed in the proportions 1:2 and 1:4 of cement B, exhibited concentric cracks, even at the first inspection, and many of them were burst across the middle;

whereas the corresponding plates from cement S were perfect. A similar result attended the inspection in the autumn of 1910; but in the meantime it had become necessary to remove the greatly damaged plates of cement B, whilst all the plates from cement S were still intact. It should also be mentioned that the plates made from cement B after raising its SO_3-content to 2.5 per cent, showed less extensive cracking than those made of the cement in its original condition, i. e., with only 0.57 per cent of SO_3.

After about 3 years' exposure of the plates to the influence of sea water, samples were taken corresponding to each mixture and each cement, with and without added gypsum, and these were analyzed at the Karlshorst laboratory of the German Portland Cement Manufacturers' Association, the shell (1 cm. thick) and core of each plate being analyzed separately. The results are set out in the subjoined Table 2, in which they have been calculated to the amount of binding medium in the mortar. In the case of cement S, both in its original condition and after enrichment to 2.5 per cent of SO_3, no change in the chemical composition of the plates could be detected as a rule; and only the 1:2 and 1:4 mortars from this cement with 2.5 per cent of SO_3 exhibited a diminution of this latter constituent in shell and core. Moreover, the percentage of lime in the shell of the 1:4 mortar (without and with added gypsum) was found to have receded a little, whilst the percentage of magnesia had increased.

TABLE I.—TESTS ON TWO PORTLAND CEMENTS OF DIFFERENT SO_3-CONTENT, AFTER HARDENING IN FRESH WATER, SEA WATER AND IN THE OPEN AIR (PERFORMED BY THE ROYAL LABORATORY FOR TESTING MATERIALS).

Tensile strength in kg per sq. cm. (cubes of 50 sq. cm. surface).

Mixture	1 cement+2 sand.			1 cement+4 sand.			1 cement+2 sand.			1 cement+4 sand.		
Kept in	Fresh water.	Salt water.	Open air.	Fresh water.	Salt water.	Open air.	Fresh water.	Salt water.	Open air.	Fresh water.	Salt water.	Open air.
Cement—	"S," as received.						"S," with SO_3-content raised to 2.5% by crude gypsum.					
After 28 days	613	573	649	268	241	291	616	588	730	348	295	388
After 1 year	656	620	855	259	251	405	875	716	821	348	236	393
Cement—	"B," as received.						"B," with SO_3-content raised to 2.5% by crude gypsum.					
After 28 days	257	278	302	109	113	143	288	254	345	112	101	143
After 1 year	365	292	441	167	133	250	434	340	598	190	149	307

Standard test (1:3:28 days in water).

	Cement "S."	Cement "B."
Tensile strength kg. per sq. cm.	28.2	20.2
Crushing strength kg. per sq. cm.	399.0	169.0
Weight per litre, poured in	1,237 grms.	1,414 grms.
Residue on 5,000-mesh sieve	15.1%	36.2%
Residue on 900-mesh sieve	2.0%	7.8%

The 1:2 and 1:4 mortars from cement B in its original condition showed a considerable decrease of lime, especially in the shell, with an enormous increase in magnesia (up to 10.8 per cent); and, in contrast to cement S, a considerable enrichment in SO_3. With cement B with 2.5 per cent of SO_3, the behavior, in spite of the increase in that constituent, was more favorable than that of the same cement in the original condition, the analysis of the plates revealing far less alteration in the chemical composition of the binding medium than in the case of the unmodified cement. The SO_3-content shows a decline very similar to that in the corresponding plates from cement S.

From the chemical composition of the plates it appears that cement S behaves equally well in sea water,

TABLE II.—CHEMICAL ANALYSIS OF CONCRETE PLATES SUBMERGED IN SEA WATER AT SYLT (ANALYSIS MADE AT THE LABORATORY OF THE ASSOCIATION, KARLSHORST).

	Percentage composition of the cements used %	Chemical composition of the binding medium in the plates. Mixture 1:2 Shell %	Mixture 1:2 Core %	Mixture 1:4 Shell %	Mixture 1:4 Core %	Percentage composition of the cements used %	Chemical composition of the binding medium in the plates. Mixture 1:2. Shell %	Mixture 1:2. Core %	Mixture 1:4. Shell %	Mixture 1:4. Core %
		Cement "S," as supplied.				Cement "S" enriched to 2.5% of SO_3 by added gypsum.				
SiO_2	23.11	22.64	22.02	21.72	22.48	22.25	21.51	22.18	20.89	22.43
$Fe_2O_3+Al_2O_3$	7.09	7.67	7.56	7.45	7.38	7.20	7.54	7.40	7.68	7.20
CaO	67.20	65.38	66.67	62.56	66.24	66.81	66.06	66.26	62.56	65.54
MgO	0.81	1.89	1.32	2.83	1.24	0.81	1.04	0.82	2.78	1.00
SO_3	1.19	0.93	0.92	1.39	1.00	2.47	1.81	1.67	2.20	1.80
Undetermined	0.60	1.49	1.51	4.05	1.66	0.46	2.04	1.67	3.89	2.03
		Free from external cracks					Free from external cracks.			
		Cement "B," as supplied.				Cement "B" enriched to 2.5% of SO_3 by added gypsum.				
SiO_2	23.43	24.04	22.16	20.14	22.57	22.39	22.06	22.90	21.73	21.70
$Fe_2O_3+Al_2O_3$	9.79	10.90	10.19	9.67	9.99	9.78	9.85	9.74	10.15	9.72
CaO	63.90	50.49	58.31	52.16	60.55	63.24	52.25	63.48	60.08	59.73
MgO	1.08	10.49	4.68	10.80	1.18	0.96	2.00	1.11	3.95	1.00
SO_3	0.57	2.74	1.36	2.12	4.69	2.43	1.60	1.65	2.01	2.75
Undetermined	1.23	1.34	3.27	5.11	1.02	1.20	2.24	1.12	2.08	5.10
		Very numerous external cracks.					Numerous external cracks.			

whether with its original or increased percentage of SO_3.

The cement B in its original condition showed the most extensive changes; but the same cement enriched to 2.5 per cent of SO_3, behaved better, although, in the opinion of such countries as prescribe a smaller percentage of SO_3, it should have proved inferior in sea water.

SUMMARY OF RESULTS:

1. The tensile tests showed that the presence of 2.5 per cent of SO_3 (sulphuric trioxide) in Portland cement is thoroughly harmless during hardening in sea water.

2. The examination of the large blocks immersed in the North Sea, and of the plates in the Wattenmeer, has shown that the cement which was richer (1.19%) in SO_3, behaved well, both in its original condition and after enrichment to 2.5 per cent of SO_3; whereas the cement with the lower SO_3-content (0.75%) and supplied specially for marine structures, behaved badly, and was even improved by enrichment to 2.5 per cent of SO_3.

3. The Chemical examination of the plates failed to reveal more than slight alterations due to sea water, in the case of the cement with the higher SO_3-content, whether in its original condition or after enrichment. The cement lower in SO_3 and used in its original condition, was found to have sustained extensive chemical changes under the action of sea water though only to a smaller extent when enriched to 2.5 per cent.

From these results it follows indubitably that the presence of up to 2.5 per cent of SO_3 in Portland cement, produces no injurious effects of any kind, whether in sea water or fresh water.

Moreover, the favorable experience that has everywhere been gained in marine construction works with cements of this kind, namely, containing a higher percentage of SO_3 than is prescribed in countries which issue special Specifications for such works, demonstrates that the higher SO_3-content of the cements in question has not led to any injurious effects in practice, provided the cement has been properly used.

Consequently, the German Portland Cement Manufacturers' Association, on the basis of the material set forth above, requests the International Association for Testing Materials to lay the following resolution before the VI Congress of the International Association, in New York, for examination and adoption:

"The Congress recommends that a uniform permissible maximum limit of SO_3, namely, 2.5 per cent, be generally adopted in Specifications for Portland Cement, whatever may be the purpose for which the cement is intended."

Printing paper, valued at not above 2½ cts. per pound, imported from Canada during the 10 months ended April 30, 1913, weighed 180 million pounds, against 50 million pounds in the previous year.

VARIOUS CHEMICAL PHENOMENA ENCOUNTERED IN THE COURSE OF INDUSTRIAL INVESTIGATIONS.*

BY J. BIED.

In the course of researches, whose immediate object is above all practical, industrial laboratories frequently come across phenomena possessing general scientific interest, which phenomena they have no time to elucidate but which may open up new fields of research by the information they afford on problems of a theoretical order.

We propose to review very briefly several phenomena of this kind, which have attracted our attention.

By means of simple and rapid experiments we endeavored to obtain some preliminary insight into the matter, but the working conditions of an industrial laboratory do not permit us to continue our investigations as far as the definite solution of such problems would entail.

We must leave the matter to others, who are equipped for scientific research or have more time at their disposal, and will now content ourselves with setting forth the results we have obtained.

DEHYDRATION TEMPERATURE OF THE SILICATES AND ALUMINATES OF LIME.

In carrying out experiments on the slaking of lime and cements by the aid of a small laboratory apparatus[1], enabling the material to be stirred up by steam and a uniform temperature of over 100° C. to be maintained, we have made the following observations:

1. Any cement that has stood the hot water test will never absorb water when treated with steam at a temperature above 140° C. This proves:

(a) That the hydrates of faintly basic aluminates and silicates cannot be formed at this temperature, and that, consequently, they cannot exist except at temperatures below 140° C.

(b) That the strongly basic aluminates and silicates are not attacked by water at this temperature, since, if they were decomposed, CaO would be liberated and an absorption of water would take place (because calcium hydroxide does not become dehydrated in an atmosphere saturated with steam, except toward the temperature of 550° C.).

2. Above 140° C., a cement that has been exposed to air naturally or artificially (by superficial

*Paper presented at the 6th Congress of the International Association for Testing Materials.

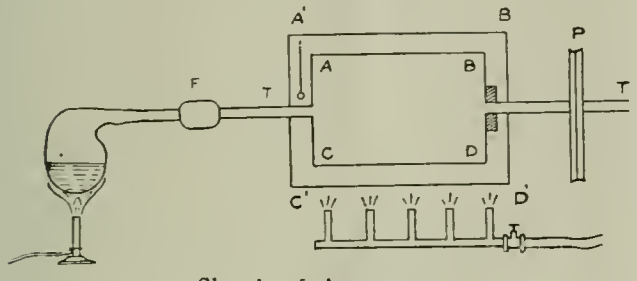
[1]The apparatus consists essentially of a first cylinder, A B C D, of copper, provided with a fixed tubulus T and a detachable one T′, fitted with a pulley F and serving for the introduction of the material. This cylinder is connected at F by means of a revolving joint, with the neck of a flask in which the water is kept in ebullition. It is surrounded by a second cylinder A′ B′ C′ D′, also of copper, made in two parts, heated by gas, and provided with thermometers which enable the temperature to be kept under constant observation. It is adapted to rotate at a speed of 5—6 revolutions per minute, the motive force being transmitted from a small hot-air motor through the pulley P. The cement under examination is placed in the cylinder A B C D, either loose or packed in small bags of open fabric. In this way it is possible to work with 50 grms. of cement and to place several kinds of cement in the apparatus at the same time, as also to prevent the fine dust from being blown away by the current of steam.

spraying and water), loses a portion of the water which has been obsorbed in the cold, namely the portion combined with the silicates or aluminates; but retains completely that portion of the water which has combined with the CaO resulting from the decomposition of the silicates, provided the treatment has taken place in saturated steam.

3. A treatment that has been baked to semi-fusion and mixed with a known quantity of quick lime, if then treated with steam at 140° C., will absorb just so much water as is needed to slake the added lime. The weight of quick lime may therefore be calculated from the quantity of water absorbed.

These three phenomena have been confirmed by Mr. B. Blount to whom we communicated our observations.

Other experiments have shown us that the decomposition and hydration temperature of the above salts differs for the silicates in comparison with the aluminates, and may be taken as about 120° for the former and 140° for the latter.



Sketch of Apparatus.

In fact:

1. A cement that is entirely siliceous, like that of Teil, does not absorb water between 110 and 120°.

2. Artificial cements containing a large proportion of alumina, will, on the contrary, absorb water at 110°, and their setting is consequently retarded considerably on that account.

3. Quick-setting cements absorb water at 110°, and their setting is retarded thereby, but as a rule they do not absorb water at 140°, their setting remaining unchanged. Some cements absorb water at 140° and nevertheless set as usual, which proves them to contain free CaO.

DETERMINATION OF FREE LIME IN CEMENTS AFTER GRINDING AND AFTER HARDENING.

The observations just recorded led us to establish very simple methods for studying the theory of decomposition and setting in cements.

Free Lime in Unaerated Cement.—The cement is heated at 450°, either in the open air, or preferably in a current of nitrogen to obviate the oxidation of the sulphur and carbon which may be present in some specimens. At this temperature the tension of dissociation of calcium carbonate is practically nil. The cement is then treated with steam at 140-150°. The amount of water fixed gives the quantity of free lime present in the cement, either as quick lime or hydroxide.

Free Lime Originally Existing in Aerated Cements.—After exposure to air, the cement is tested as above, to determine the total content of CaO. It is then exposed to the air afresh, to cause it to take up x% of water, either by spraying in the cold or by exposure to wet steam below 100°.

On then treating the second specimen with steam at above 140°, one can ascertain the quantity of water that has been combined by the silicates out of a total quantity absorbed by the cement. From this result it is easy to deduce the initial quantity of free lime in the cement under examination.

For instance, assuming that a cement containing a certain quantity of water (A), loses a certain quantity of water (a) on being treated by steam at 140°, and is made to absorb a quantity of water (B).

At 140° it loses a quantity of water (a + b), b being the quantity of water combined by the silicates (or aluminates), and B — b the quantity of water combined by the lime resulting from the decomposition of these latter during the operation of exposure to air to which the cement has been subjected, and during which it has absorbed the total quantity (B).

The water combined by the lime resulting from the first decomposition is therefore:

$$X = (B - b)\frac{a}{b}.$$

Consequently:

$$A - (X + a) = A - B\frac{a}{b}$$

is the water originally combined by the initial free lime in the cement in question.

It should be noted in passing that, by operating on synthetic products, one can deduce from these phenomena the reactions of decomposition and the formula of the hydrated silicates and aluminates.

Lime Freed During Hardening.—The moisture (uncombined water) is expelled from the hardened cement, by drying at 100-110° until the weight is constant.

The carbon dioxide is determined, and the loss on heating at 450° is ascertained, on the dried cement, as above, which enables the total combined water (water of hydration of the aluminates, silicates and lime) to be calculated. The calcined cement is exposed to steam at 140°C., the resulting increase in weight giving the amount of water combined by the free lime. It is then easy to calculate how much calcium hydroxide in the hardened cement corresponds to the amount of water combined at 140° by the calcined cement, which calcium hydroxide originates in the initial free lime and from the decomposition of the silicates. The former of these values, however, could be determined beforehand. On the other hand the amount of carbon dioxide combined is known.

It is true that these determinations may become complicated when the cement contains other volatile

matters besides carbon dioxide and water: such for example as unconsumed carbon, alkalis, etc., or when it contains substances that are liable to increase in weight on calcination, such as sulphides, ferrous oxide, etc., which combine with oxygen and thus falsify the loss on calcination.

Such cases are, however, exceptional, and in any event the process is applicable to the theoretical investigation of the setting of limes and cements.

We have also investigated the liberation of calcium hydroxide as hardening progresses; and we believe we have found that this liberation is far more gradual than is generally supposed, and that a large proportion of active, undecomposed product remains in the hardened cement, even when aged.

SILICATE COMBINED WITH LIME AT 1000° C.

With the same apparatus we have endeavored to ascertain which is the first compound of silica and lime that is formed at about 1000° C.—by determining the free lime on the one hand and the combined silica on the other.

For the determination of silica in combination with lime in a baked product, we have adopted the Le Chatelier method, which we have employed for a number of years and which has always furnished highly concordant comparative results.

It consists in treating the total silica (rendered insoluble by evaporation and calcination at 150-180°) with a 3 per cent solution of caustic potash for ¼ of an hour at boiling heat—which dissolves the whole of the silica which was combined with the lime—and by weighing the residual sand, the weight of which latter, deducted from the total silica, furnishes the weight of combined silica. By determining on the other hand at over 140° (as above), the amount of water required to slake the residual free lime, we obtain the formula of the silicate formed.

It is thus that, with a good siliceous limestone (containing less than 2 per cent of alumina and iron), we have obtained, by this process:

Limestone calcined at	Silicate formed
1,000° C.	SiO_2, 2.5 CaO
1,200° C.	SiO_2, 2.6 CaO

It would seem therefore as though the basic silicates were formed at even the lowest kiln temperatures.

BICALCIUM SILICATE.

The experiments of Day Allen, Shepherd and Rankin have demonstrated the existence of three allotropic modifications of bicalcium silicate.

α = stable above 1,400° C.,
β = stable between 600 and 1,400° C.,
γ = stable in the cold.

This last form is pulverulent, and is inert from the hydraulic point of view.

The form a, cooled suddenly by immersion in mercury, would be hydraulic.

We repeated the quenching experiments in the following manner. Tablets having the composition of bicalcium silicate with 2 to 3% of R_2O_3, were baked at between 1600 and 1700°. They were taken out of the furnace and quenched suddenly (some in mercury, the others in cold water), or else cooled in the air.

As indicated by the American workers, quenching prevents the pulverization which, on the other hand, occurred normally in the case of all the tablets cooled in the air.

The quenched tablets were triturated and mixed with water, and then made up into test pieces which were kept under water.

At the end of a year of such storage, none of these test pieces had acquired any appreciable strength.

This observation is contrary to the opinion generally held at the present time on the hydraulicity of quenched bicalcium silicate.

FUSED CEMENTS.

By baking natural or artificial alumino-calcareous products, we have obtained fused products, which pour perfectly, are liquid towards 1450°, and when triturated, furnished slow-setting hydraulic products, which, however, harden very rapidly in all cases, the pure paste having, for example, a tensile strength exceeding 60 kilos. at the end of two days.

These products do not exhibit any expansion in hot water.

They had the formula of monocalcium aluminate (the iron and silica being regarded as impurities). When treated with water they set slowly, but became very quick setting on addition of calcium hydroxide. It would seem that monocalcium aluminate sets by simple rehydration, like gypsum, but that it cannot exist at the ordinary temperature in presence of lime, with which it combines rapidly. Nevertheless, it cannot be used as puzzolane, since bicalcium aluminate is decomposed by calcium sulphate.

On the contrary, monocalcium aluminate hardens on the addition of gypsum, gives high tensile strengths and seems to be incapable of being decomposed.

Finally, I should like to direct the attention of investigators to the fact that I have succeeded in producing, and use as a lining for certain furnaces, a cement that is absolutely stable under hot water tests. The analysis is as follows:

SiO_2, siliceous	1.15
SiO_2, combined	20.25
Al_2O_3	2.00
Fe_2O_3	1.62
CaO	71.50
MgO	1.70
CO_2	....
SO_3	traces
Volatile matters	0.20
Undetermined	1.58
	100.00

Sugar-refining profits in Australia by the large company operating there were $1,135,000 for the six months ended March 31, 1913, half of which was earned in Fiji and New Zealand. A 10 per cent dividend absorbed $730,000 and a $1.20 per share bonus, $183,000.

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NOTES AND COMMENTS.

Pennsylvania Coke Record.

Pennsylvania stands pre-eminent among the States in the production of coal and in the manufacture of coke. The quantity of coke produced in the state in 1912 was 27,372,018 short tons, valued at $56,054,478, against 21,923,935 tons, valued at $43,053,367, in 1911, according to Edward W. Parker, of the United States Geological Survey. The increase in 1912, compared with 1911, was 5,448,083 short tons, or 24.85 per cent, in quantity, and $13,001,111, or 30.2 per cent in value. The quantity of coke made in 1912 was the largest on record, exceeding the previous maximum of 26,513,214 tons in 1907 by 858,804 short tons, but falling behind the earlier year in value by $11,583,546.

As a producer of coke Pennsylvania is relatively of greater importance than as a producer of coal, for whereas, including the production of anthracite, Pennsylvania contributes less than half the entire output of coal in the United States, nearly two-thirds the total production of coke is made within that state. Pennsylvania has, however, not progressed as fast as some other states in the matter of conserving the by-products of coke making. All but a very small quantity of the state's coke is made in beehive ovens or in rectangular ovens in which the process is one of partial combustion, as in the beehive ovens, and without recovery of by-products or utilization of the heat generated in the coking process.

We thus note slowness of an established industry in the adoption of new processes. Notwithstanding the recent progress in coke manufacture as noted in another place in this issue, half the coke in the country is made with no reference to these improvements and the resulting savings.

Potash Importations.

The importation of "potash salts" for consumption into the United States during 1912 amounted to 622,179,164 pounds, valued at $10,692,285, according to W. C. Phalen, of the United States Geological Survey. This importation is only a part, however, of the potash salts entering the United States. To it should be added the importation of kainite and "manure salts," including "double manure salts." The imports of potash salts of these classes amounted to nearly 700,000 long tons, valued at more than $4,000,000. The imports for consumption of materials entering largely into the fertilizing industry, plus the domestic phosphate rock, reached the total valuation of over $46,000,000. These statistics in detail, together with others showing the condition of the German potash and salt industry, are given in the Geological Survey's report on potash just issued as an advance chapter of the volume "Mineral Resources of the United States" for 1912.

Ton of Coal Makes More Coke Than Formerly.

The quantity of coal required to produce a ton of coke is much less than formerly. The average gain in 1912 compared with 10 years ago is probably at least 160 pounds. It is doubtful if in the earlier years the actual yield of coal in coke exceeded 60 per cent, whereas in 1912 it was 67 per cent, according to the United States Geological Survey. This gain is largely due to the increase in the production of by-product coke, in which the yield of coke from a ton of coal is very much higher than in making beehive coke.

In Illinois, Indiana, Massachusetts, Michigan, New Jersey, New York and Wisconsin, where coke is made exclusively in by-product plants, the yield varies from 69.6 per cent (in Wisconsin) to 81.8 per cent (in Indiana), whereas in the states where beehive practice prevails the yield in 1912 varied from 50 per cent (in Georgia) to 66.5 per cent (in Pennsylvania).

Advance in Making By-Product Coke.

It is now 20 years since coke was first manufactured in by-product ovens in the United States. By this process all the products of the coal are conserved—first of course the coke, but also large quanti-

ties of coal tar, ammonia, gas, and other constituents. It is asserted that in the by-product coke plants of the present day the by-products pay the cost of the process—that is, that the coke is clear gain. The old method of coke-making, by means of the beehive oven, which is in fact still largely in use, allows all these valuable by-products to waste absolutely.

The first plant using the by-product or retort type of oven was installed at Syracuse, N. Y., in May, 1893, according to Edward W. Parker, of the United States Geological Survey. This pioneer plant consisted of 12 Semet-Solvay ovens and produced in that year 12,850 tons of coke. The plant has since been increased to 40 ovens. The second by-product plant to be constructed was one of 60 Otto-Hoffmann ovens at Johnstown, Pa. From these small beginnings the by-product branch of the coking industry has grown steadily, new plants being added each year until at the close of 1912 there were 5,061 ovens of this type in operation and the production of retort coke for the year was 11,048,489 tons, or a little more than one-fourth of the total output. The making of by-product coke has materially developed along other lines than in the simple building of new ovens and increased production. The ovens of the present day are larger, higher, and wider than those installed in earlier times. The charging capacity of the original ovens at Syracuse was 4.4 tons of coal and the time required for coking was 24 hours. Even at that time a gain of at least 50 per cent in coking time was obtained compared with beehive practice, which required 48 hours for the production of furnace coke and 72 hours for the production of foundry coke.

The Semet-Solvay ovens of to-day hold at the average about 16 tons of coke. The exact capacity depends, of course, on the specific gravity of the coals used. The original 60 Otto-Hoffman ovens at Johnstown had a charging capacity of about 5½ tons each. The latest installation of United Otto ovens at Mayville, Wis., in 1912, have an average capacity of 10.33 tons of coal each. The coking time has been materially reduced, so that excellent furnace coke is now made in 16 to 18 hours. The development of modern mechanical appliances has also done much to forward the efficiency of the retort oven and to reduce the labor necessary per unit of output. The same crew of men who 20 years ago were required to handle 25 of the small ovens and who were carbonizing say 110 tons of coal a day are able with modern equipment to handle 50 or more of the larger ovens, coking 1,000 tons of coal a day. This represents an increase of about nine-fold in the tonnage carbonized per man employed. These developments have been accompanied by marked improvements in by-product recovery in the manufacture of ammonia and other by-products. Twenty years ago the only ammonia recovered was in the form of crude liquor running from 12 to 15 per cent ammonia. Now coking plants are producing ammonia liquor ranging from crude through the different grades required for the manufacture of flameless powder, etc., to the production of almost chemically pure aqua ammonia, at one operation. Still another marked development in by-product oven practice is in the adaptation of the surplus gas to the illumination of cities and towns. In the earlier days the ovens produced only a small and irregular quantity of surplus gas of varying quality. To-day by-product ovens in the United States are selling from 40 to 50 million cubic feet of gas a day for illuminating purposes. Almost the entire supply of gas in some cities is derived from retort ovens. Among these cities may be specially mentioned Boston, Mass.; Camden, N. J.; Indianapolis, Ind.; Hamilton, Ohio; Baltimore, Md.; Duluth, Minn.; South Chicago, Ill.; and Milwaukee, Wis.

Until 1908 the Semet-Solvay and United Otto (Otto-Hoffman) ovens held the entire field of retort-oven practice. In that year, however, the Illinois Steel Co. constructed at Joliet, Ill., the 140 Koppers regenerative by-product ovens. This plant was doubled in the following year and a number of other plants of this type have since been constructed in different parts of the country. In 1909 construction was begun on 300 Didier ovens at South Bethlehem, Pa., but they had not been put into blast at the close of 1912. During 1912 a bank of 22 Klönne ovens were completed at Muncie, Ind. At this plant all the gas from the ovens is supplied to the city of Muncie. The ovens are heated with producer gas made from the coke. Two recent installations of Semet-Solvay ovens, one at Waukegan, Ill., and the other at Indianapolis, Ind., are constructed on the same plan.

The Analysis of Black Powder and Dynamite.

The Analysis of Black Powder and Dynamite is the title of Bulletin No. 51, recently issued by the United States Bureau of Mines. This bulletin outlines the methods of analysis that are used by the Bureau of Mines in the examination of certain classes of explosives. The present form of most of these methods has been worked out in the bureau's explosives laboratory. The methods employed by Prof. C. E. Munroe were taken as a basis, and were elaborated to meet the demands incident to the treatment of complicated mixtures and to the development of the explosives' art. A subsequent bulletin will discuss the methods of analysis of "permissible" explosives, many of the latter being of decidedly complicated character and requiring special treatment. This bulletin presents the methods of analysis of "ordinary" dynamite, and the ammonia, gelatin, low-freezing, and granular dynamites, and the common grades of black gunpowder and black blasting powder. The bulletin is published by the bureau for the information of all persons interested in explosives and their safe and efficient use in mining work.

As the term "ordinary" dynamite, though much

used, has no conventional meaning, and may be used to cover a wide variety of compositions of matter, it may be noted that the standard dynamite used at the Pittsburgh testing station is a good example of the "ordinary" dynamite known in this country. This testing station dynamite has the following composition:

COMPOSITION OF PITTSBURGH TESTING STATION DYNAMITE.

	Per cent.
Nitroglycerin	40
Sodium nitrate	44
Wood pulp	15
Calcium carbonate	1

As most permissible explosives contain only the constituents found generally in the various types of ordinary dynamite, the chemist will usually find it possible to analyze such explosives either wholly or partly by following the general methods of analysis here given for the type of explosive that seems most closely related to the one under examination.

Flavor of Butter Injured by Metals.

Economic conditions make it necessary at present to hold butter in storage from the summer season, when it is plentiful, to the winter season, when it is scarce. If the butter is properly made this can be done without materially injuring its quality. It often occurs, however, that butter which has been held in storage for some months develops disagreeable flavors that greatly lessen its value. These bad flavors that will often pass unnoticed when the butter is fresh may become so serious a defect after three or four months in storage as to render the butter almost unsalable. The chemical changes which cause these bad flavors are often too small to be detected by the ordinary analytical methods of the laboratory, but the senses of smell and taste are far more delicate, and as soon as bad flavors are detected by them the value of the product is lessened.

Some metals either cause or greatly accelerate certain bad flavors in butter, although most of the experiments along this line have not included storage butters. Recently the scientific staff of the Dairy Division of the Bureau of Animal Industry in the United States Department of Agriculture has reported that the presence of very small amounts of iron in cream causes certain undesirable flavors to increase in intensity during storage. These flavors are often designated by butter experts as "metallic," "oily," or "fishy." The injurious effect of iron was found by adding iron in known quantities, varying from 1 to 500 parts, to a million parts of cream. The butter made from such cream was compared with that made from cream where all precautions were taken to avoid any undue contact with iron during the whole process of butter making. The butter was stored at 0° to 10° Fahrenheit, and the quality of the butter was scored by experts at different times. In every instance when the butter was scored a few days after making, the samples to which iron had been added scored lower than the butter made from cream which contained no iron. This held true in most cases on the second and third scoring, which occurred at intervals varying from 20 to 187 days. The most noticeable feature was the rapid development of bad flavor in the butter containing the iron. When both the control and the experimental butter became fishy it was noticed that the control butter was the last to become so. There was a marked oily flavor present in most samples that subsequently became fishy. Only a small proportion of the iron added to the cream was found in the butter, the remainder having been taken up by the buttermilk and wash water.

Butter was also made from cream which had stood in rusty cans, and in every case this butter had a peculiar taste and was easily picked out from all other samples. The buttermilk also had a decided metallic taste.

The influence of copper on the flavor of butter was studied in a similar manner, and it was found that copper, even in small quantities, seemed to cause more marked changes of flavor in butter than did the iron, with a decided tendency toward a fishy flavor in storage. Two experiments showed very plainly the harmful effect of using poorly tinned pasteurizers, even though the cream came in contact with the copper surface for only a few seconds, for, aside from this, all other conditions were exactly alike during the complete process of butter manufacture.

This work shows that if cream is kept in rusty cans or comes in contact with iron or copper at any time during the process of butter making it may take up iron or copper from rusty cans, exposed bolt heads, or other metal parts of pasteurizers or churns, in sufficient quantities to affect the flavor of storage butter. Though there is nothing to show that the nature of the flavor is appreciably changed, it does demonstrate very clearly that the rate of development of the undesirable flavor is greatly accelerated during storage by very small quantities of either iron or copper.

RECENT PATENTS.

The following patents relating to industrial and engineering chemistry are reported by C. L. Parker, solicitor of chemical patents, McGill Building, Washington, D. C.:

1,055,617. Manufacture of *Stannic Chloride*. William F. Doerflinger, New York, N. Y., assignor, by mesne assignments, to Niagara Alkali Company, a Corporation of New York. Patented March 11, 1913.

1,055,701. *Pigment* and process of Making Same. Rene Bohn, Mannheim, Germany, assignor to Badische Anilin & Soda Fabrik, Ludwigshafen-on-the-Rhine, Germany, a Corporation. Patented March 11, 1913.

1,055,727. Method of Producing Hydrates of *Stannic Chloride*. William F. Doerflinger, Huntington, N.

Y., assignor, by mesne assignments to Niagara Alkali Company, a Corporation of New York. Patented March 11, 1913.

1,056,031. *Fire-Clay* Substitute. Peter Kinander, Charleston, Mississippi. Patented March 18, 1913.

1,056,125. Method of Treating *Metals*. Auguste J. Rossi and William F. Meridith, Niagara Falls, N. Y., assignors to The Titanium Alloy Manufacturing Company, New York, N. Y., a Corporation of Maine. Patented March 18, 1913.

1,056,161. Process for Producing Fermentable *Sugars*. Francis E. Gallegher, Newton, Mass., assignor to Standard Alcohol Company, New York, N. Y., a Corporation of Maine.

1,056,219. Preparation of *Opium Alkaloids*. Karl F. M. Schaerges, deceased, Basel, Switzerland, by Magdalena Schaerges, assignor to Hoffman-La Roche Chemical Works, New York, N. Y. Patented March 18, 1913.

1,056,277. Composition for Tempering *Steel*. Truman H. Houser, Dorranceton, Pa. Patented March 18, 1913.

1,056,311. Process for Extracting *Precious Metals* from Their Ores. Sidney Williams, San Francisco, California. Patented March 18, 1913.

1,056,365. *Explosive* and Process of Producing Same. Fritz Raschig, Ludwigshafen-on-the-Rhine, Germany. Patented March 18, 1913.

1,056,382. Method of Producing *Lead Hydrate*. Theodore G. Timby, Chicago, Illinois. Patented March 18, 1913.

1,056,389. *Explosive*. Louis G. M. Adinau, San Francisco, California, assignor to L. Adinau Company, a Corporation of California. Patented March 18, 1913.

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PRELIMINARY REPORT FOR THE COMMITTEE ON COAL ANALYSIS OF THE AMERICAN SOCIETY FOR TESTING MATERIALS AND THE AMERICAN CHEMICAL SOCIETY.*

(Concluded from July Issue.)

Moisture.

By W. F. Hillebrand, Chairman.

In view of our own experience and that of the chemists who coöperated with a subcommittee of the International Committee on Analyses,[9] it seems needless to strive at present in ordinary work for a very high degree of refinement in the determination of moisture. So sensitive are coals to humidity changes of the air that it is evidently only by chance that two or more analysts will reach the same results for moisture in a given coal, especially if they live in different cities or make the tests on different days in the same place. To the truth of this the report of the above-mentioned International Committee bears abundant testimony. The variations therein shown are probably due, in part, to lack of realization on the part of many of the analysts of the magnitude of the changes in moisture content that may arise during the transfer of the coal from the containing vessel to the drying receptacle and during the weighing operation. Nevertheless, the chances of variation are so serious that the opening statement above is fully justified.

A. APPROXIMATE METHOD.

Use a pair of shallow weighing capsules with ground caps or other well-fitting covers. Suitable forms are indicated below. Heat these under the conditions at which the coal is to be dried, stopper or cover, cool over concentrated sulphuric acid for 30 minutes and weigh.

Dip out with a spoon or spatula from the container two portions of coal of about 1 gram weight each, put these quickly into the drying vessels, close, and weigh at once.

An alternative procedure (more open to error), after transferring an amount slightly in excess of 1 gram, is to bring to exactly 1 gram weight (±0.5 mg.) by quickly removing the excess weight of coal with a spatula. The utmost dispatch must be used in order to minimize the exposure of the coal until the weight is found.

Further procedure:

(*a*) *For Anthracite and Bituminous Coals.*

Quickly place the vessels open in a preheated oven (at 104-110° C.) through which passes a current of air dried by concentrated sulphuric acid. Close the oven at once and heat for one hour. Then open the oven, cover the capsules quickly and place in a desiccator over concentrated sulphuric acid. When cool, weigh.

(*b*) *For Sub-bituminous and Lignitic Coals.*

Instead of air use a current of dry carbon dioxide, both for the preliminary heating of the capsules as well as for the drying of the coal. After an hour's heating, open the oven, cover the capsules and place them in a vacuum desiccator over concentrated sulphuric acid. Exhaust the desiccator to remove the carbon dioxide from the capsules. When cool, slowly let in dry air and weigh at once.

Notes on Method A.—(1) Although watch glasses ground to fit, and with clamp, are most effective drying vessels on account of their shallowness, it is probable that glass capsules as used by S. W. Parr and as recommended by the International Committee will be found most convenient. The capsules themselves should be about 2½ cm. wide and 1½ cm. deep. The shallower they are, consistent with convenient handling, the quicker and more perfect the drying. The Parr capsules have the upper part of the wall ground on the outside and the cap is ground on the inside, leaving a smooth edge, a feature which facilitates transfer of the coal to the ashing vessel.

A porcelain cup (Eimer and Amend, No. 2657) is preferred at the Bureau of Mines, where it is used with a well fitting aluminum cover. It has the disadvantage of greater depth as compared with the glass capsule, but if demand arose this defect could be remedied. Its only advantage over the glass capsule lies in permitting the ash determination to be made on the moisture sample without transfer.

(2) The oven must be so constructed as to have a uniform temperature in all parts and a minimum of air space. The air current must be rapid enough to renew the gas in the oven frequently when the oven holds from 6-12 vessels of coal.

[9] Proceedings 8th Intern. Congr. Appl. Chem., 25, 41.

The cylindrical form of oven shown in *Technologic Paper* 8, of the Bureau of Mines, p. 5, and holding 6 crucibles, is well adapted for the purpose; also a new rectangular oven of the same Bureau, holding 12 crucibles and measuring inside 1½ in. high by 4 in. wide and 14½ in. long. The approximate air space in each of these ovens is 0.05 cubic foot. With this type of oven, of small air space, it has been found at the Bureau of Mines that the air must be renewed from 2 to 4 times a minute to obtain the maximum loss in weight from the coal in 1 hour.

S. W. Parr uses an oven 12 in. in each of the three directions, and here the renewal of air need not be so rapid, 8 to 10 times in an hour being probably sufficient.

(3) Although carbon dioxide is absorbed by coal at room temperature there is no absorption above 100° C. The need for modifying the procedure for sub-bituminous and lignitic coals arises from the fact that such coals undergo very many times the amount of oxidation that Appalachian coals suffer. Nitrogen gas is to be preferred to carbon dioxide because its density is so near that of air that it will be unnecessary to displace it from the capsules before final weighing. If this gas is used, a vacuum desiccator is unnecessary.

(4) The International Committee in its report recommends, when using air, to remove one of the capsules from the oven at the expiration of 30 minutes, to continue heating the other for 30 minutes longer, and to accept the higher loss in weight, if a difference is shown, as may happen with certain coals. Our committee has not deemed it advisable to adopt this precaution, both on account of the added labor involved in testing four portions of a sample instead of two and because the probable error in the determination of the true moisture content is so large as to render the precaution of doubtful value.

B. METHODS OF GREATEST ACCURACY.

(1) Heat as in Method A, but in a current of dry nitrogen that is free from oxygen. Instead of a shallow vessel a U-tube with well ground stoppers may be used, which tube can be hung in an oven at the temperature of 104-110°. Fill the tube with nitrogen before taking its weight empty, and weigh always with a counterpoise tube of about the same displacement and weight. Introduce about a gram of the coal quickly through a short and wide-stem funnel without attempt to secure a weight of exactly 1 gram. Before hanging the tube in the preheated oven pass nitrogen to displace all air, and continuously while heating. When the last trace of moisture has disappeared from the outlet of the tube, remove from the oven and let cool with the gas still passing. When cool close the cocks, hang in the balance case for 15 minutes and after opening one cock weigh with the counterpoise. The counterpoise need not be filled with nitrogen.

As a check the water given off may be collected in sulphuric acid and weighed, care being taken to keep the absorption vessel full of nitrogen. The weight of water thus obtained is a little higher than that found indirectly.

Ba. ALTERNATIVE METHOD (FOR USE WHEN TIME DOES NOT PRESS).

Dry in a vacuum desiccator over sulphuric acid of maximum concentration for 3 and 7 days, longer if necessary.

The vacuum should be high—not over 3 millimeters of mercury pressure—and should be checked by a manometer. The capsules mentioned above may be used. Before evacuating fill the desiccator with an inert gas, and before opening the desiccator carefully let in air dried by sulphuric acid. Weigh immediately.

This method is easy of execution and is sound in principle since a possible error due to loss of gaseous constituents is negligible.

It has not been deemed advisable to recommend the xylene method of Constam (boiling a large weight of coal with xylene and collecting and measuring the water that distils over) since, though promising, the method has not been subjected to exhaustive test.

ALLOWABLE VARIATIONS.

	Same analyst. Per cent.	Different analysts. Per cent.
Moisture under 5 per cent	0.2	0.3
Moisture over 5 per cent	0.3	0.5

Volatile Matter.

By S. W. Parr, Chairman.

It is recommended that for volatile matter determinations a 10-gram platinum crucible be used having a capsule cover, that is, one which fits inside of the crucible and not on top. The crucible with one gram of coal is placed in a muffle maintained at approximately 950° C. for 7 minutes. With a muffle of the horizontal type, the crucible should not rest on the floor of the muffle but should be supported on a platinum or nichrome triangle bent into a tripod form. After the more rapid discharge of the volatile matter, well shown by the disappearance of the luminous flame, the cover should be tapped lightly to more perfectly seal the cover and thus guard against the admission of air.

ALTERNATIVE METHOD.

One gram of coal is placed in a platinum crucible of approximately 20 cc. capacity (35 mm. in diameter at the top and 35 mm. high). The crucible should have a capsule cover which will readily adjust itself to the inside upper surface of the crucible. The crucible is placed in the flame of a Méker burner, size No. 4, having approximately an outside diameter at the top of 25 mm. and giving a flame not less than 15 cm. high. The temperature should be from 900° to 950° C. determined by placing a thermocouple through the perforated cover which for this purpose

may be of nickle. The junction of the couple should be placed in contact with the center of the bottom of the crucible. Or the temperature may be indicated by the fusion of pure potassium chromate in the covered crucible (fusion of K_2CrO_4, 940° C.). The crucible is placed in the flame about 1 cm. above the top of the burner and the heating is continued for 7 minutes. After the main part of the gases have been discharged the cover should be tapped into place as above described.

For lignites a preliminary heating of 5 minutes is carried out, during which time the flame of the burner is played upon the bottom of the crucible in such a manner as to bring about the discharge of volatile matter at a rate not sufficient to cause sparking. After the preliminary heating the crucible is placed in the full burner flame for 7 minutes as above described.

ALLOWABLE VARIATIONS.

	Same analyst. Per cent.	Different analysts. Per cent.
Bituminous coals	0.5	1.0
Lignites	1.0	2.0

Determination of Ash.

By S. W. Parr, Chairman.

In any outline for the determination of ash the attempt must be made to meet the conditions of the widely varying mineral constituents of coals. Those of the Illinois type perhaps have disturbing constituents in greatest amount. These are (a) calcium carbonate, (b) iron sulphate, (c) iron pyrites.

Concerning the extent to which carbonates are present, out of 500 samples of Illinois coal examined, only 9 per cent were found to have calcium carbonate present in an amount less than 0.2 per cent. Very nearly half of the samples have this constituent in excess of 1 per cent. One-fifth of the samples have more than 2 per cent of calcium carbonate and a very considerable number were found to have over 4 per cent with a few isolated cases reaching as high as 10 per cent of calcium carbonate in the raw coal.

Concerning the distribution of sulphate, investigations show this constituent practically always present and in the form of ferrous or ferric sulphate. In the fresh coal the amount varies from a few tenths up to 1 per cent. There is a rapid increase in the content of sulphate in the laboratory sample ground to 60 mesh. In a large number of cases examined, the amount of this constituent had doubled during six months of laboratory storage. An examination of the samples which had been retained in storage in the buckwheat size without fine grinding showed that the increase in sulphate was practically confined to the finely divided particles; that is to say, in that part of the sample which will pass a 60-mesh screen practically all of the increase in sulphate is found. That part of the sample which is retained on a 20-mesh and which passes through a 10-mesh has very little if any increase in sulphate, and the next larger size has so little increase that it may be considered as having the normal content as found in the vein sample.

As to sulphur in the form of sulphide it must be looked upon as an additional element of disturbance in the presence of calcium carbonate, for the reason that any temperature adequate for burning off of carbon will result in the burning also of the sulphur to sulphur dioxide and part or all of the calcium carbonate to calcium oxide. Under these conditions calcium sulphate is inevitably formed. If this reaction were complete or definite in amount, the proposition would be much simplified. An additional point to be observed is the fact that calcium oxide may further increase in weight from absorption of sulphur from the gas flame.

In the final method for ash determination the following items should be borne in mind.

First. Calcium carbonate begins rapid decomposition at and above 900°; below that temperature the decomposition is partial but evident at temperatures above 600° C., or a dull red, and must be considered.

Second. Calcium oxide in the presence of iron pyrites readily takes up sulphur and retains the same in the form of calcium sulphate. Attention should be called in this connection also to the fact that where calcium oxide is present the sulphur from the gas flame may be readily absorbed, with the formation of calcium sulphate.

Third. If high temperatures are maintained during the process of burning off the carbon the quantity of sulphate is seriously modified by reduction in the presence of red-hot carbon.

Fourth. Temperatures which are carried to the fusion point will further modify normal constituents by the formation of calcium silicate and the liberation of sulphur trioxide.

Fifth. Ferrous sulphate is decomposed at 550 to 600° C. and ferric sulphate at 700° C. With the temperature necessary for burning off the carbon there is likely to be a transfer of sulphur trioxide to the calcium oxide. The decomposition of calcium sulphate does not occur rapidly below 1100° C. in the absence of carbon, but may occur to a disturbing extent at 900° C. or above.

Sixth. Sulphur in the form of iron pyrites is completely oxidized at the low temperatures indicated, along with the burning out of the carbon. If it is so discharged it does not operate to disturb the values by uniting with calcite, but in so far as calcium oxide develops, it is retained.

METHODS FOR DETERMINING ASH.

Unless the coal is of a type known to be free from carbonates the amount of carbon dioxide must be determined. A five-gram sample, recently boiled distilled water and dilute hydrochloric acid are employed, making use of any convenient apparatus for collecting, absorbing and measuring accurately the carbon dioxide discharged from the coal. It is most convenient to obtain the factor as in the form of carbon.

One gram of coal, either freshly weighed or that which has been used for the moisture determination, is ignited in a shallow capsule or porcelain crucible by placing directly in a muffle maintained at a dull or cherry-red temperature between 700 and 750° C. and retained at this temperature for 20 or 30 minutes or until all of the carbon is burned out. The capsule is cooled in a desiccator and weighed. In the absence of a muffle the desired temperature may be obtained by placing the capsule at first just above the tip of a Bunsen flame turned down to about 2 or 3 inches in height. After the larger part of the carbon is burned off in this manner the flame is increased so that the tip comes well into contact with the bottom of the capsule.

For coals having carbon dioxide present in an amount to exceed 0.2 per cent, the ash after cooling is moistened with a few drops of sulphuric acid (diluted 1:1) and again carefully brought up to 750° C. and retained at that temperature for 3 to 5 minutes. The capsule is cooled in a desiccator and weighed. Three times the equivalent of carbon present as carbon dioxide is subtracted from the ash as weighed in order to restore the weight of the calcium sulphate formed to the equivalent of calcium carbonate.

A full discussion of the determination of ash will be published soon.

CORRECTED ASH.

The application of a correction for sulphur present in the iron pyrites depends largely upon the use to be made of the results. For technical purposes it may well be omitted. For comparative purposes, especially where use is to be made of the pure coal or unit values, it should be applied. Five-eighths of the sulphur present in the pyritic form if added to the ash would restore the iron sulphide to the original form as weighed.

While with certain types of coal, especially those extensively used for steaming purposes, averaging 15 to 20 per cent ash, it is evident that there is a volatile ash constituent of considerable importance due to hydration of clayey material, in our present state of information as to the uniform distribution of this constituent it does not seem advisable to incorporate it in technical analyses. For a comparative study, however, a correction for this type of ingredient cannot be avoided. The factor which has received extended application is an increase of 8 per cent of the ash as weighed to represent this volatile constituent.

ALLOWABLE VARIATIONS.

	Same analyst. Per cent.	Different analysts. Per cent.
No carbonates present	0.2	0.3
Carbonates present	0.3	0.5
Coals with more than 12 per cent ash	0.5	1.0

Sulphur.

By Perry Barker, Chairman.

In view of the close agreement of results obtained in the experimental work on various types of coal, the subcommittee recommends that a choice of the following three methods for the determination of sulphur be permissible:

(a) The Eschka method.

(b) The Atkinson method of fusion with sodium carbonate.

(c) The method of fusion with sodium peroxide in the Parr calorimeter bomb.

I. THE ESCHKA METHOD.

The essentials of this method as described by G. L. Heath[10] have been modified as given in the former report of the committee of the American Chemical Society on Coal Analysis.[11] Additional directions for application when city gas is used are also included in the method herein recommended.

Thoroughly mix on glazed paper 1.3737 grams of coal and 6 grams of Eschka mixture. This mixture is prepared by thoroughly incorporating two parts of magnesium oxide with one part of sodium carbonate by passing through a 40-mesh screen. By this method of preparation the mixture attains a uniformity comparable with that of the laboratory sample of coal and thorough incorporation is, therefore, more easily effected. Transfer to a No. 1 Royal Berlin porcelain crucible and cover with about two grams of the Eschka mixture.

On account of the amount of sulphur contained in artificial gas, it is preferable to heat the crucible over an alcohol, gasoline or natural gas flame or in an electrically heated muffle. Heat the crucible, placed in a slanting position on a triangle, over a very low flame to avoid rapid expulsion of the volatile matter, which tends to prevent complete absorption of the products of combustion of sulphur. Heat the crucible slowly for about 30 minutes, gradually increasing the temperature and occasionally stirring until all black particles disappear, which is an indication of the completeness of the procedure.

The use of artificial gas for heating the coal and Eschka mixture is permissible, provided the crucibles are heated in a muffle and a blank determination of the amount of sulphur absorbed from the gas is made.

Place the crucible in a cold gas muffle and gradually raise the temperature to about 870° or 925° C. (cherry-red heat) in about one hour. Maintain this maximum temperature for about one and a half hours and then allow the crucible to cool in the muffle. Remove and empty the contents into a 300 cc. beaker and digest with 200 cc. of hot water for one-half to three-quarters of an hour, with occasional stirring. Filter and wash the insoluble matter by decantation. After several washings in this manner, transfer the insoluble matter to the filter and wash five times, keeping the mixture well agitated. Treat the filtrate, amounting to about 250 cc. with 10 to 20 cc. of saturated bromine water and make slightly acid with concentrated hydrochloric acid Transfer the beakers to the hot plate and, upon boiling, precipitate the soluble

[10] J. Am. Chem. Soc. 20, 630.
[11] Ibid. 21, 1127.

sulphates by adding slowly from a pipet with constant stirring 10 cc. of a hot 10 per cent solution of barium chloride. Continue boiling for fifteen minutes and allow to stand for at least two hours at a temperature just below boiling. Filter through an ashless filter paper and wash first with hot water containing 1 cc. of hydrochloric acid per liter and then with hot distilled water until a silver nitrate solution shows no precipitate with a drop of the filtrate. Place the wet filter containing the precipitate of barium sulphate in a weighed platinum or alundum crucible, allowing a free access of air by folding the paper over the precipitate loosely to prevent spattering. The paper should be smoked off gradually at first. After the paper is practically consumed raise the temperature to approximately 925° C. and heat to constant weight. In case artificial gas is used as a heating agent, a blank to correct for contamination due to sulphur in the gas is carried through the process in the manner described above, using the same amounts of Eschka mixture, wash water, bromine water, hydrochloric acid and barium chloride solution as employed in the regular determination. A large number of tests using a mixed coal and carburetted water gas containing not more than 25 grains of sulphur per 100 cubic feet show blanks averaging 0.003 gram of barium sulphate. These blanks include the impurities in the form of sulphur compounds in the reagents, which amount to nearly one-half of the total weights. The percentage of sulphur is obtained by deducting the blank, provided artificial gas is used, and multiplying the resulting figures by ten.

II. THE ATKINSON METHOD.[12]

Thoroughly mix on glazed paper 1.000 gram of the laboratory sample of coal with 7 grams of dry sodium carbonate and spread evenly over the bottom of a shallow platinum or porcelain dish. Place on a triangle slightly elevated above the bottom of a cold muffle. Raise the temperature of the muffle gradually until a temperature of 650° to 700° C. (dull red heat) has been obtained in half an hour and maintain this temperature for ten or fifteen minutes. The sodium carbonate should not sinter or fuse. The mixture should not be stirred during the heating process. When the dish has cooled sufficiently to handle, the matter should be examined for black particles of unburned carbon and in case such indications of incompleteness of the process appear, the dish should be replaced and heated for a short time. When all carbon is burned, remove the dish and digest the contents with 100 to 125 cc. of warm water. Allow the insoluble matter to settle, decant through a filter and wash several times by decantation. Transfer to the filter, adding a few drops of a solution of pure sodium chloride, if the insoluble matter tends to pass through the filter. The washing should be continued until the filtrate shows no alkaline reaction. Make the filtrate slightly acid with sufficient concentrated hydrochloric acid and precipitate the sulphates with barium chloride as described under the Eschka method. No oxidizing agent is required.

III. THE PEROXIDE FUSION METHOD.

This method is most conveniently carried out in the bomb which is a part of the Parr calorimeter.[13] The sodium peroxide and potassium chlorate used in the fusion mixture should be of the grade especially prepared for the determination of heating values with this apparatus.

Before mixing the coal and chemicals for the fusion, thoroughly dry the bomb and warm slightly in order to be sure that all traces of moisture have been removed. Place one gram of potassium chlorate, about ten to twelve grams of specially prepared sodium peroxide and one-half gram of the laboratory sample of coal, which has previously been air-dried, in the bomb and seal quickly to avoid the absorption of moisture by the sodium peroxide. Shake the bomb thoroughly and rap sharply on the laboratory table to remove the portions of the mixture which may adhere to the top of the bomb on the terminals. Place in a vessel containing sufficient water to completely submerge the portion of the bomb containing the mixture, allowing the stem to protrude sufficiently to attach the terminals of the ignition circuit. Ignite the wire with a current of 15 to 20 volts either from a lighting circuit, four-cell storage battery or four or five dry cells in series. After the bomb has cooled, remove, dry, and open over a 4-in. watch glass placed on top of the beaker in which the fusion is to be dissolved. The bottom of the bomb is removed and the fused mass is knocked out upon the watch glass with the special rod furnished with this apparatus. The portions of the fusion which adhere to the sides and top of the bomb are washed into the beaker with hot water, the remainder of the fused mass is added and completely dissolved. The solution is acidified with hydrochloric acid in such a manner as to give approximately 5 cc. of free acid in the entire volume, which should amount to 250 to 300 cc. of liquid. Heat the solution, filter through a qualitative filter and wash several times with hot water. Heat the filtrate to boiling and precipitate the soluble sulphates by slowly adding 10 cc. of the hot solution of barium chloride. Continue the boiling for fifteen minutes and allow to stand for at least two hours at a temperature just below boiling. Filter, wash and ignite as described under the Eschka method. Particular care should be taken in washing the precipitate obtained by this method in order to remove all of the soluble salts which are formed in the fusion process.

Experimental Results.—The above recommendations have been made after careful consideration of all the available methods for the determination of sulphur in coal. In order to make careful tests of such

[12] J. Soc. Chem. Ind., March 29, 1886. J. Iron and Steel Inst., No. 2 (1896). J. Am. Chem. Soc. 21, 1128 (1899).

[13] A simpler, inexpensive bomb is described in Am. Chem. J., 25, 184 (1903); see also Noyes, "Organic Chemistry for the Laboratory," p. 21.

methods, a number of samples were prepared which represented various types of coal having sulphur contents ranging from one to four per cent. The results of comparative tests for the various methods are given in Table I. This same set of samples was submitted to two other members of the committee for comparative tests. One member employed the Eschka method essentially as given in this report while the other followed the Peroxide Fusion method. The results of these determinations, together with the original figures from Table I for the various methods are given in Table II.

In connection with the report on the various methods for the determination of sulphur in coal, the results of comparative tests by a member of the committee[14] are of particular interest. The results of these tests on 35 samples of coal show an average difference of 0.02 per cent of sulphur between the Peroxide Fusion method and the Eschka method on the samples which averaged slightly over two per cent of sulphur. The average results from the bomb washings were 0.16 per cent lower than by the Peroxide Fusion method, while the results by the special Photometric method were 0.11 per cent lower than by the Peroxide Fusion method.

After careful consideration of the various methods, together with the data which are given herewith, the subcommittee recommends that the method of precipitation from bomb washings be discarded and endorse a choice between the (1) Eschka method, (2) the Atkinson method and (3) the method of fusion with sodium peroxide in the Parr calorimeter.[15]

TABLE I—COMPARATIVE TESTS.

Determination of sulphur in coal by various methods. Percentages refer to dry coal basis.

Sample.	I.	II.	III.	IV.	V.	VI.	VII. (a)	VII. (b)
1	1.02	0.000	1.01	1.00	1.03	1.06	1.01	1.02
2	1.99	0.017	2.00	2.02	1.94	2.01	1.79	1.92
3	2.98	0.004	3.02	2.99	2.93	3.04	3.00	3.13
4	3.95	0.019	3.97	3.96	3.87	3.94	3.91	3.94
(Dup.)	3.96							

I. Eschka method. Samples heated in gas-fired muffle, corrected for blank determination due to sulphur in gas, which averaged 0.025 per cent. This process is regularly in use in the laboratory where these tests were made.

II. Residual sulphur on extracting residue from Eschka method with hydrochloric acid.

III. Eschka method, according to methods for coal analyses adopted by the American Chemical Society in 1899, using the alcohol lamp.

IV. Atkinson's fusion method: "Method of Fusion with Sodium Carbonate," J. Am. Chem. Soc., 21, 1128.

V. Precipitation from washings obtained by combustion in oxygen bomb calorimeter.

VI. "Parr's Method of Combustion and Fusion in Bomb with Sodium Peroxide," this journal, 1, 689 (1909).

VII. "Precipitation of Soluble Sulphates from Washings Resulting from Combustion of Coal in Oxygen Bomb Calorimeter by means of Barium Hydrate and Subsequent Neutralization and Titration with Standard Alkali and Acid," Z. Chem. Apparatenkunde, 2, 542; (a) and (b) are duplicate determinations on same sample.

TABLE II.

Determination of sulphur in coal (results on standard samples). Percentages refer to dry coal basis.

Sample.	Eschka method. Table I.	Eschka method. Analyst A.	Peroxide fusion method. Table I.	Peroxide fusion method. Analyst B.
1	1.02	1.03	1.06	1.02
2	1.99	1.98	2.01	2.01
3	2.98	2.92	3.04	3.01
4	3.95	3.86	3.94	4.03

ALLOWABLE VARIATIONS.

	Same analyst. Per cent.	Different analysts. Per cent.
For coal	0.05	0.1
For coke	0.03	0.05

Determination of the Calorific Power.

By H. C. Dickinson, Chairman.

The specifications are to be of two classes, (a) and (b). The procedure specified under (a) may be followed in tests where a tolerance of at least 1 per cent is allowed. The procedure under (b) is to be used in all cases where the limit of tolerance is less than 1 per cent, and is to be followed in all cases of dispute. Under (b) any three determinations made at the same time on the same sample may be required to fall within a range of 0.3 per cent.

Combustion Bombs.—The Atwater, Emerson, Mahler, Peters, Williams or similar bombs may be used. For (a) the lining material of the bomb need not be specified. The Parr calorimeter may also be used, but only on condition that both parties to the contract agree to its use. For (b) the bomb shall have a lining of platinum, gold, procelain enamel or other material which is not attacked by nitric and sulphuric acids, or other products of combustion.

Calorimeter Jacket.—The calorimeter (except the Parr) must be provided with a water jacket, having a cover to protect the calorimeter from air currents. The jacket must be kept filled with water. For (b) the water in the jacket must be kept within 2 or 3 degrees of the temperature of the room and should be stirred continuously by some mechanical stirring device.

Stirring of the Calorimeter Water.—The water in the calorimeter must be stirred sufficiently well to give consistent thermometer readings while the temperature is rising rapidly. The speed of stirring should be kept constant. For (b) a motor-driven screw or turbine stirrer is recommended and the speed should not be sufficient to hold the temperature of the calorimeter more than 0.3° or 0.4° C. above that of the jacket, when the stirrer is allowed to run continuously. Accurate results cannot be obtained when too much energy is supplied by the stirring device or

[14] The Journal of Industrial and Engineering Chemistry, 1, 689 (1909).

[15] Mr. Fieldner recommends that precipitation from the bomb washings be permitted when both parties agree to its use, especially for coals used for steaming or heating purposes.

when the rate of stirring is too irregular. The portion of the stirring device immersed in the calorimeter should be separated from that outside by nonconducting material, such as hard rubber, to prevent conduction of heat from the motor or outside air.

Thermometers.—Thermometers used shall have been certified by a government testing bureau and shall be used with the corrections given on the certificate. This shall also apply to electrical resistance or thermoelectric thermometers. For (b) correction shall also be made for the temperature of the emergent stem of all mercurial thermometers, and for the "setting" of Beckmann thermometers. For accurate work either Beckmann or special calorimetric thermometers graduated to 0.01° or 0.02° are required. Such thermometers should be tapped lightly just before each reading to avoid errors due to the sticking of the mercury meniscus, particularly when the temperature is falling. A convenient method is to mount a small electric buzzer directly on the top of the thermometer and connect it up with a dry cell and a push button. The button should be pressed for a few seconds immediately before each reading.

Oxygen.—Oxygen used for combustions shall be free from combustible material and for (b) it shall not contain more than 5 per cent nitrogen and argon together. The total amount of oxygen contained in the bomb for a combustion shall not be less than 5 grams per gram of coal. But the combustion must be complete as shown by the absence of any sooty deposit on opening the bomb after firing.

Firing Wire.—The coal in the bomb may be ignited by means of either iron or platinum wire. If iron wire is used, it should be of about No. 34 B. & S. gauge and not more than 10 cm. (preferably 5 cm.) should be used at a time. A correction of 1,600 calories per gram weight of iron wire burned is to be subtracted from the observed number of calories. Except however, that this correction may be omitted from both the standardizations of bomb and coal combustions, provided the same amount of wire is used in all cases.

Standardization.—The water equivalent of a calorimeter can best be determined by the use of standard substances such as the standard combustion samples supplied by the Bureau of Standards. The required water equivalent is equal to the weight of the sample multiplied by its heat of combustion per gram and divided by the corrected rise in temperature.

The calorimeter shall be standardized by the combustion of such standard samples supplied by the Bureau of Standards, and used according to the directions given in the certificates which accompany them. A standardization shall consist of a series of not less than five combustions of either the same, or different standard materials. The conditions as to amount of water, oxygen, firing wire, method of correcting for radiation, etc., under which these combustions are made shall be the same as for coal combustions. For (b) in the case of any disagreement between contracting parties a check standardization shall be made at the time of test, but such standardization may consist of two or more combustions of standardizing samples.

Manipulation.—1. *Preparation of Sample:* The ground sample, which is in approximate moisture equilibrium with the atmosphere, is to be thoroughly mixed in the bottle and an amount, approximately one gram, is to be taken out and weighed in the crucible in which it is to be burned. Coals which are likely to be blown out of the crucible should be briquetted. Standardizing samples are also to be briquetted. After weighing, the sample should preferably be immediately placed in the bomb and this closed. This procedure is necessary to avoid sublimation when naphthalene is used.

2. *Preparation of the Bomb.*—The firing wire, if iron, should be measured and coiled in a small spiral and connected between the platinum terminals, using if necessary, a piece of platinum wire somewhat heavier than the iron wire, to make the connection. The platinum and the iron must both be clean. About ½ cc. of water should be placed in the bottom of the bomb to saturate, with moisture, the oxygen used for combustion. When the crucible is put in place in the bomb, the firing wire should touch the coal or briquet of standard material. For the combustion of standardizing samples iron wire is preferable to platinum.

3. *Filling the Bomb with Oxygen.*—Oxygen from the supply tank is to be admitted slowly to avoid blowing the coal from the crucible, and the pressure allowed to reach 20 atmospheres for the larger bombs or about 30 atmospheres for the smaller bombs, so that the bomb shall contain an amount of oxygen sufficient for complete combustion, viz., at least 5 grams per gram of coal, or other combustible. When feasible, the bomb may be exhausted before filling to remove the nitrogen of the air, thus reducing the amount of the nitric acid formed.

4. *Calorimeter Water.*—The calorimeter is to be filled with the required amount of water, depending upon the type of calorimeter. The amount may be determined either by measurement in a standardized flask or by weighing. For (b) distilled water should be used and the amount determined by weighing. The amount must be kept the same as that used in standardization of the apparatus, or a correction applied for the difference in weight.

5. *Temperature Adjustments.*—The initial temperature in the calorimeter should be so adjusted that the final temperature, after the combustion, will not be more than 1 degree, preferably about ½ degree, above that of the jacket, under which conditions the total correction for heat gained from or lost to the surroundings will be very small when the rise of temperature is 2° or 3°, and the effect of evaporation will also be small.

6. *Firing Current.*—The electric current used for firing the charge should be obtained from storage, or dry cells having an E. M. F. of not more than 12 volts.

The circuit should be closed by means of a switch which should remain closed for not more than two seconds. When possible, it is recommended that an ammeter be used in the firing circuit to indicate when the firing wire has burned out. For (b) the E. M. F. of the firing battery shall not exceed 12 volts, since a higher voltage is liable to cause an arc between the firing terminals, introducing additional heat, which cannot be measured with certainty.

7. *Method of Making an Observation.*—The bomb when ready for firing is to be placed in the calorimeter, the firing wires connected, the cover put in place and the stirrer and thermometer so placed as not to be in contact with the bomb or container. The stirrer is then started and after the thermometer reading has become steady, not less than two minutes after the stirrer is started, temperatures are read at one-minute intervals for five minutes and the charge is then fired, noting the exact time of firing. Observations of temperature are then made at intervals depending upon the method to be used for computing the cooling correction. When the temperature has reached its maximum and is falling uniformly, a series of thermometer readings is taken at one-minute intervals for five minutes to determine the cooling rate.

8. *Titration.*—After a combustion the bomb is to be opened, after allowing the gas to escape, and the inside examined for traces of unburned material or sooty deposit. If these are found the observations shall be discarded. If the combustion appears complete, the bomb is to be rinsed out and the washings titrated to determine the amount of acid formed. A correction of 230 calories per gram of nitric acid should be subtracted from the total heat observed. If the sulphur content of the coal is determined the amount of sulphuric acid should be computed and an additional correction of 1,220 calories per gram of H_2SO_4 should be subtracted, for the excess of the heat of formation of the sulphuric acid over that of nitric acid.

Computation of Results.—The following method of computation is recomended, to take the place of the Pfaundler or other similar formulas for computing the cooling correction (radiation correction).

Observe (1) the rate of rise (r_1) of the calorimeter temperature in degrees per minute for four or five minutes before firing, (2) the time (a) at which the last temperature reading is made immediately before firing, (3) the time (b) when the rise of temperature has reached six-tenths of its total amount (this point can generally be determined by adding to the temperature observed before firing, sixty per cent of the expected temperature rise and noting the time when this point is reached), observe (4) the time (c) of a thermometer reading taken when the temperature change has become uniform some five minutes after firing (5) the final rate of cooling (r_2) in degrees per minute for five minutes.

The rate r_1 is to be multiplied by the time $b - a$ in minutes and tenths of a minute, and this product added (subtracted if the temperature were falling at the time a) to the thermometer reading taken at the time a. The rate r_2 is to be multiplied by the time $c - b$ and this product added (subtracted if the temperature were rising at the time c and later) to the thermometer reading taken at time c. The difference of the two thermometer readings thus corrected, provided the corrections from the certificate have already been applied, gives the total rise of temperature due to the combustion. This multiplied by the water equivalent of the calorimeter gives the total amount of heat liberated. This result, corrected for the heats of formation of nitric and sulphuric acids observed and for the heat of combustion of the firing wire when that is included, is to be divided by the weight of the charge to find the heat of combustion in calories per gram. Calories per gram multiplied by 1.8 give the B.t.u. per lb. *See example.

The results should be reduced to calories per gram or B.t.u. per pound of dry coal, the moisture being determined upon a sample taken from the bottle at about the same time as the combustion sample is taken.

For an accurate comparison of different coals from the calorimeter determinations it is evident that the results should be reduced in each case by the heat of evaporation (preferably at 20° C.) of the water formed by combustion of the coal, since in the bomb

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*EXAMPLE.

Observations.

Water equivalent 2550 g.
Weight of charge 1.0535.
Approximate rise of temp. 3.2°.
60 per cent of approximate rise 1.9°.

Time.	Temp.	Corrected temp.
10-21	15.244°	(Thermometer corrections from the certificate)
22	.250	
23	.255	
24	.261	
25	.266	
(*a*)26	.272	15.276°
	Charge fired.	
(*b*)27-12	17.2°[1]	

[1]The initial temperature is 15.27°; 60 per cent of the expected rise is 1.9°. The reading to observe is then 17.2°.

(*c*)31	18.500°	18.497°
32	.498	
33	.497	
34	.496	
35	.494	
36	.493	

Computation.

r_1=0.028°÷5=0.0056° per minute. $b-a$=1.2 minutes.
The corrected initial temperature is
15.276°+0.0056°×1.2=15.283°.
r_2=0.007°÷5=0.0014° per minute; $c-b$=3.8 minutes.
The corrected final temperature is 18.497°+
0.0014×3.8 ..... =18.502°
Total rise 18.502°—15.283°..... = 3.219°
Total calories 2550×3.219 ..... = 8209
Titration, etc. ..... = —7

Calories from 1.0535 grams coal..... 8202
Calories per gram..... 7785

Or B.t.u. per lb..... 14013

In practice, the time $b-a$ will be found so nearly constant for a given calorimeter with the usual amounts of fuel that b need be determined only occasionally.

ALLOWABLE VARIATIONS.

	Per cent.		Per cent.
Same analyst	0.3	Different analysts	0.4

this water is condensed and the heat of condensation is included in the measurement, while in nearly all commercial conditions the water vapor passes off uncondensed and the heat is lost. On account of the additional time required to determine the hydrogen content of the coal samples the correction necessary to reduce to the above basis or "net" heat of combustion is not generally applied, although it may amount to several per cent in extreme cases.

Combustion of Anthracites and Coke.—For anthracites and coke, which have a high ash content and do not readily burn completely, the following procedure is recommended:

The inside of the crucible is lined completely with ignited asbestos in a thin layer pressed well down into the angles. The coal is then sprinkled evenly over the surface of the asbestos. Otherwise the procedure is as previously described.

Parr Calorimeter.—The essential conditions for the operation of the Parr or peroxide calorimeter are as follows:

The coal should be finely pulverized. While 60 mesh is sufficient for bituminous coals, anthracites should be ground to at least 100 mesh.

The sodium peroxide used should be received in solder-sealed tins and of a size suitable for emptying completely into the container for use, preferably a glass jar with lever-sealed cap.

In addition to the reaction the peroxide serves as a diluent and the ratio necessary for a quiet reaction should be maintained preferably 0.5 gram of coal to approximately 10 grams of peroxide. One gram of pulverized potassium chlorate is also used to advantage. It is first thoroughly mixed with the coal in such a manner as to avoid any possibility of lumping of these two substances. A thorough and uniform mixing with the peroxide is then assured by shaking in the closed cartridge.

Coals with moisture above 2 or 3 per cent must be oven-dried at 110° C. in the usual manner after weighing out, and before mixing with the chemicals.

The correction factors to be subtracted are as follows:

For each per cent of ash	0.00275° C.
For each per cent of sulfur	0.005° C.
For 1 gram of $KClO_3$	0.130° C.
For electric fuse wire	0.008° C.
For oxygen of bituminous coals for 0.5 gram	0.025° C.
For oxygen of brown lignites for 0.5 gram	0.050° C.
For oxygen of benzoic acid for 0.5 gram	0.121° C.

The products of combustion, CO_2 and H_2O, combine with the chemical with the formation of heat, which amounts in each case to 27 per cent of the total heat of the reaction.

The corrections for ash, fuse wire, etc., in terms of the temperature rise together with radiation and thermometer corrections must first be subtracted from the indicated rise in temperature. The formula for the final calculation then becomes:

$$\frac{\text{Corrected thermometer rise} \times 0.73 \times \text{total water}}{\text{0.5 gram coal}} = \text{calorific value}$$

SYNTHESIS OF PRECIOUS STONES.*

By I. H. LEVIN.

Our present success in reproducing the precious stones makes us reflect upon the unsuccessful attempts of the alchemists to produce the precious metals. How much our modern ways differ from theirs! The so-called magic and mysticism of the alchemists have given way to science. Selfish competition and lack of co-operation have given way to accumulation of knowledge and experience and the free exchange of information among contemporaries. Desire simply to get a product has given way to real search for knowledge and the discovery of laws and principles. The solitary lives and the cherished secrets of the alchemists have made way for the free and open world-wide movements and interchange of ideas that have made our times such an age of industry, and to take one example from out of the many, have made it possible for a contemporary, or a follower, to crown with success the efforts of groups of men that have labored to reproduce the precious stones.

Of the precious stones, the diamond, the emerald, the ruby, and the sapphire have all been successfully synthesized. Only the ruby and the sapphire, however, have outgrown the laboratory stage of production, and are fast becoming important members of the field of chemical industry. The less precious stones, amethysts, garnets, tourmalines, etc., have not appealed to the chemists because they are not valuable enough as natural products. The pearl, though a true precious stone, is almost altogether of animal origin. Only the diamond, the emerald, the ruby, and the sapphire will be considered in this paper. It will be helpful to consider the characteristics common to all the precious stones before tracing the development of the production of these stones through their checkered careers.

The precious stones owe their value mostly to the permanence of their beauty. The beauty is due to their intrinsic composition and to the way the stones are made to affect light by being cut in certain forms. The permanence is due to their hardness and to the fact that the stones are chemically inert and resist corrosion. To be sure, extraneous conditions, such as custom and rareness, may affect their value. In the case of the gray diamond of Africa, the bort, and the hardest known diamond, the black diamond of Brazil, the carbonado, we have the only instance of the precious stones being very valuable when not beautiful.

Color, whenever found in the gems, is due to impurities which are usually minute quantities of the metallic oxides. Various colors in the different precious stones can be produced by the same oxide, and the same color in the different precious stones has been traced to different oxides.

*Presented at the meeting of the New York Section of the American Chemical Society, May 24, 1912.

The precious stones are transparent crystalline varieties of very common minerals. The diamond may be considered as the chef d'oeuvre of the earth's work on carbon. The ruby and the sapphire are part of the large family, corundum, of which the ordinary emery stone is a very humble relation. Stones identical in composition with the emerald are so common at Limoges that the mineral is said to be used as paving blocks.

Each of the precious stones may be made to lose some or all of its characteristics—its color, crystalline structure, transparency, and even hardness—and be made to return to common clay, so to speak. On the other hand, the "common clay" may be reacted upon in such ways that it may take on all the properties of the precious stones.

Research along the lines of the precious stones has been most profitable when emphasis was placed on experiments that would lay bare the conditions that are necessary to produce the stones rather than on those which would merely bring about products. In the case of the diamond and the emerald these conditions are not known; in the case of the ruby and the sapphire they are so well understood that the making of these has now formed part of the ever-growing field of chemical industry.

THE DIAMOND.

The transformation of diamond to graphite or carbon has been accomplished again and again. The process has also been reversed and some few diamonds have been produced by various investigators. Nevertheless, no interpretation of the phenomena has, as yet, been given. The work of Moissan[1] is extremely interesting, but not enlightening. He obtained his clue from the analytical work of Friedel.[2]

The Devil's Canyon was once littered with meteorites. Some of these found their way over to France and when analyzed by Friedel tiny diamonds were found imbedded in the mass of iron. Moissan tried to reproduce the conditions of the fiery meteor. In an electric furnace he placed a carbon crucible containing pure iron and very pure carbon. The carbon dissolved in the molten iron until a saturated solution was formed, and while the material was at white heat he plunged it in a bath of molten lead or mercury. The sudden cooling caused tremendous internal pressure and the liquid carbon was crystallized into diamonds. The products were microscopic, but were hard, showed the crystalline form, and on chemical test proved to be diamonds. One little fellow weighing about 6 mg., when burned in oxygen produced about 23 mg. of carbon dioxide. Theoretically, 22 mg. should have been produced.

The high dispersion of light—which is twice as great as that of glass—gives to the diamond its so-called "play of fire." In addition to this property the diamond reflects almost all the rays of light that strike its surface and give it the characteristic luster known as adamantine. To these properties, accentuated by the lapidary's art, the diamond owes its beauty. The chemical inertness of the gem has made it possible for the stone to conserve its beauty through the ages. The diamond, most valuable when colorless, is found, however, in very many colors.

THE EMERALD.

Chemically, the emerald is a metasilicate of aluminum and glucinum, $Al_2Gl_3(SiO_3)_6$. Hautefeuille and Perry,[3] 1890, dissolved the constituents of the gem in their relative proportions in a bath of dimolybdate of lithium and keeping the bath at 800° C. for fifteen days, succeeded in crystallizing out tiny emerald crystals. A little chromic oxide was used to give the green color. These crystals are in every way perfect, but too small, the largest being only 2 mm. long and 1 mm. wide, and 1 mm. thick. They were very expensive, much more so than the earth-made product.

Beyond this successful laboratory attempt, no one has, up to the time of this writing, made public the making of, if made at all, the emerald on an industrial scale. The experiment of Hautefeuille and Perry, though extremely interesting, is not very instructive, and, as with the diamond, we are not much nearer to knowing what are the conditions necessary to be attained to make the emerald.

The emerald owes its value to its green color and resembles the color of the grass in the spring. The common beryl is a golden yellow. The emerald is identical with it in every respect, save color. This difference is due simply to the presence of different impurities. Almost all the rays of light impinging upon the surface of an emerald enter it, and very few are reflected from its surface, very much as in the case of glass. Furthermore, the emerald is not as optically dense as the diamond. We have, therefore, neither the metallic luster nor the "play of fire" as in the diamond. However, there resides in the emerald a rich, soft, green color that gives to the stone a charm that is to some much more fascinating than the brilliancy of the diamond.

THE RUBY.

The ruby was the first of the precious stones to be synthesized on a commercial scale and has a more fascinating history than either the emerald or the diamond. Chemically speaking, it is simply the oxide of aluminum with a trace of chromic oxide, to which it owes its rich pigeon-blood color. The natural product has traces of other impurities that play a rôle that seems to us, in our present lack of knowledge, to be far out of proportion to their actual size. The synthetic product is ofttimes ruined in the making by quantities of impurities that are so small that they can scarcely be detected by analytical methods. Cor-

[1]See Comp. rend., 1892, 1893, 1894, 1895, 1896 (le four electrique).
[2]Friedel, "Sur l'existence du diamant dans le fer meteorique du Canon Diabolo," Comptes rendues de l'Academie des Sciences, 114, 1037, Dec. 12, 1892.
[3]Annales de chimie et de physique, 1890, 6 serie, tome XX, pages 447, etc.

undum is often free from the oxide of chromium and we have either a colorless stone, or, if some other oxides are present, we may have a blue stone—the sapphire—or shades of green, yellow, smoky tinges, etc. As an example of the traces of impurities in the natural product, note the effect of radium emanations on some of the earth-made rubies, sapphires, and colorless corundum, and the non-effect of the emanations on the synthetic rubies and colorless corundum. (The effect of radium on the synthetic sapphires has not yet been ascertained). F. Bordas using radium bromide of 1,800,000 activity turned rubies into brick-red color, white into brown and black, and blue stones into greenish to yellowish tinged stones. The synthetic stones were not affected. These very same transformations have been produced by the writer in the case of some synthetic rubies and colorless corundums by the admixture of a trace of the same impurity in each of the stones. (The influence of this material plays so great a part in the industry that I hope the non-mention of same will be excused).

Crystalline transparent alumina can be crystallized out of molten baths, can be condensed as crystals from its gaseous state, and can be "frozen" into crystals from the molten state.

The most interesting attempt to crystallize alumina out of molten baths was that of Frémy and Hautefeuille. The oxides of lead, aluminum, and chromium were fused in a large crucible for about seven to eight days in a furnace used for glass-making. Masses of rubies from 30 to 40 kilos were sometimes obtained, but among these not a ruby was found that was thick enough to be of any value as a gem. One of the crystallographic axes developed more than another, and only thin, laminated crystals were produced.

The attempts to condense the alumina vapor produced similar useless crystals, judged from the view point of gems. About this time we have a new generation interesting itself in the same problem. Frémy worked with a number of collaborators, during 1877-1890. They found that alumina and hydrofluoric acid, on being heated, would cause the aluminum fluoride formed to be reacted upon by the water vapor produced and condense as corundum. As they were originally written, we have

$$Al_2O_3 + 6HF = 2AlF_3 + 3H_2O$$
$$2AlF_3 + 3H_2O = Al_2O_3 + 6HF$$

At that time there was only a suspicion that there were such phenomena as chemical equilibria (writing the previous reaction thus:

$$6HF + Al_2O_3 \rightleftarrows 2AlF_3 + 3H_2O$$

the reversibility of the reaction and the existence of the equilibrium is easily noticed).

But the platinum ware to carry out the above was too costly, and Frémy and Feil, and later Frémy and Verneuil, carried on a series of brilliant experiments with ordinary sand crucibles. It was found that in the presence of vapor of K_2CO_3 amorphous alumina would be changed into corundum. Sand crucibles were filled in the following manner: Alumina, K_2CO_3, and Cr_2O_3 were mixed with fine charcoal, which was packed around a core composed of alumina and CaF. Upon gently heating, the charcoal escaped as CO_2 and made the mass porous. Each tiny hole became a nest, as it were, where a tiny ruby was born. The slower the process, the larger the rubies that were produced. Carrying on the process in only eight days the largest stone produced was 4 to 5 mm. long and about 1 mm. thick, weighing about one-third carat, or 60 mg. To produce larger stones the process would have to be carried on infinitely slower. If the assumption be correct that a large stone could thus be made, the product would be, of course, very interesting, but the process much too costly.

Thus the corundum crystallized out of molten baths or condensed from vapors produced only thin, laminal crystals. These not only were too thin to be cut into gems, but lacked the beauty of the earth-made product which appears to be made up of a series of layers. The light coming through these layers enriches itself and gives to the ruby its wealth of color.

Rubies are made to-day by fusing alumina in the oxyhydrogen flame and permitting the molten mass to solidify in the cooler zones of the flame. With the introduction of the oxyhydrogen torch of St. Clair Deville, experiments were begun. Here, again, Gaudin turned his attention to the synthesis of the ruby. He succeeded in fusing quartz which has a melting point slightly higher than corundum with the oxyhydrogen flame. He tried for thirty years to fuse alumina into corundum but without success. So long as the material was in the flame it was transparent, but the alumina cooled into opaque masses when the flame was removed. Gaudin[4] in his last memoire concluded that it was impossible for him to produce transparent corundum by using only alumina because of the great tendency of the substance to devitrify (become opaque). Moreover, alumina melts at a very high temperature without passing through a pasty state. It suddenly becomes fluid like water and then vaporizes and rapidly disappears like camphor.

The matter was given up for about fifteen years, for there was little hope proffered for its fulfillment. It then happened that rubies appeared on the market whose origin could not be accounted for. It was explained that a mine was discovered near Geneva. As a matter of fact, a curate, or priest, succeeded in fusing chips of natural rubies given him by the lapidaries of Geneva, into large stones. If ruby chips could be fused, then Al_2O_3 could. This latter, Verneuil[5] succeeded in accomplishing after many years of labor, and developed the process so that rubies could be made that were large in size, good in color, and at sufficient speed to make the industry possible.

A modified inverted oxy-hydrogen torch of Deville

[4]Compt. rend., 69, 1343.
[5]Annales de chimie et de physique, 8, serie II (1894).

is used as the starting point in modern practice. It produces a flame of many zones varying in temperature from 1900° to 2400° C. The torch consists of two concentric tubes; the inner tube carries the oxygen, extends about a foot beyond the outer and has a cylindrical shaped top. In the lower portion of the torch, the outer or hydrogen carrying tube extends an inch or two beyond the oxygen tube. The ruby forming powder is placed in a sieve bottom box which, in turn, is screwed into the cylindrical top of the oxygen tube.

When the torch is lit, a little hammer is caused to knock periodically on the top of this box, and particles of alumina are thus blown into the flame. In the beginning of the process, the flame is comparatively cold and just heats an earthenware rod that is so placed as to catch this powder. As the powder continues to fall on this rod it forms a pyramid of fritted alumina. The heat is gradually increased until the top of this pyramid becomes molten and a tiny stalk, so called pin-head, begins to grow. At this stage the flame is made still hotter and the powder falls in molten drops upon this pin-head. Each succeeding drop falls upon a larger base until an unflawed pear shape, or so-called ruby boule, is produced.

This boule is one single crystal with the optical axes directly perpendicular to one another. When the stem of this boule is broken the stone breaks in two. The great difficulties encountered by Prof. Verneuil in his early attempts were because of this peculiar nature of the stone. Accidentally he obtained a small boule formed on a long, straight stem, and for many years afterward failed to reproduce the same result. The rubies that he tried to make were all formed on a very wide base, and upon cooling broke into tiny particles.

Pure alumina is one essential of this process. The presence of 0.0005 of 1 per cent of a certain impurity is sufficient to absolutely discolor the ruby, and produce a brick-red instead of the pigeon-blood stone. In our making of alumina a very interesting state of equilibrium occurs, the ignorance of whose presence caused a loss for a short time of about 16 per cent of the product. There are many technical details connected with the getting of pure alumina. Suffice it to say that the material must be extremely pure, for every impurity has a tendency to ruin the product by either spoiling the color or making the material brittle. The delicacy of the entire process may be inferred from the above.

The stone cut from a boule is in every way similar to the natural ruby. Physically and chemically these stones are identical. There is perhaps but one method of telling the synthetic from the natural stone, and that is that in the natural stones the imperfections have flat bounding sides and are so-called negative crystals; the imperfections in the synthetic stones have round surfaces and are simply air bubbles which in many cases can be detected only by a powerful magnifying glass. Both the natural and the synthetic stones are made up of a series of successive layers. In the case of the synthetic stone, one can realize from the way it is made, the layers are curved; the natural product has flat parallel layers.

THE SAPPHIRE.

It will be remembered that the synthetic ruby industry first started with reconstructed stones. Sapphire chips, however, can not be fused into reconstructed sapphires in a similar way because the color disappears. This phenomenon was excellent material for half-baked interpretations with corresponding results.

We took up the research on the sapphire in our laboratory in Paris in 1909 with Prof. Verneuil as chief chemist.

The sapphire owes its blue color to the presence of minute quantities of the oxides of iron and titanium; however, up to the synthesis of the sapphire, there exists no complete analysis showing both of these oxides to be present in the gem.

The method employed in the research was, in brief, the making of corundum beads or boules by means of Prof. Verneuil's torch and method of fusion, and studying the coloring properties of the various oxides. The research was further correlated with the earth-made product with past experiences in pure and applied chemistry. The view point was necessarily always taken from the only means at hand to produce corundum beads. The history of the gem, such as the duration of time, temperature, and pressure that the earth might have employed, was, of course, an enigma, so that the view point taken to correlate the gem with the products that might be made in the laboratory was that the sapphire was simply an earth-made bead, blue in color, etc. Although the melting point about 1870° C., and boiling point of corundum are quite close, still, by Verneuil's method of fusion, some phenomena of corundum solutions may be observed and interpreted. In this way the research was brought in line with past chemical experiences with the result that many reactions could be predicted. The production of blue articles in ceramics, or other fused products of industry, or the occurrence of blue in the fusion of any of the alumina materials, such as bauxite, or any high temperature reaction which produced bluish colored products, especially those in which the oxides of interest played a part, were carefully investigated. In this way the research was further correlated with past chemical experiences.

Some of the negative results following the various clues were, nevertheless, quite interesting, but only a few can be mentioned here. In the majority of cases the clues followed gave positive results. In some of the experiments of Sainte Claire Deville and Carron[6] to obtain the ruby, blue patches were obtained, and it was believed by them that the sapphire owed its blue color to a lower oxide of chromium. Successive experimenters, however, failed to realize any blue color by the use of some of the oxides of chromium. The cobalt

oxides, which are used so extensively in ceramics to produce blue, can not, for some reason or other, be retained in the corundum. By the addition of materials such as CaO, blue stones are obtained which are, however, not genuine, synthetic sapphires.

In Gintl's[7] work on the fusion of bauxite in the electric furnace, some blue patches of corundum were made which showed, on analysis, to consist of TiO_3, 0.65; FeO, 0.79; MnO, 0.50; CaO, 1.83; MgO, 0.35; NaO, 2.07; SiO_2, 12.28; Al_2O_3, 81.88. Scoria in the blast furnaces are sometimes blue, and owe their color to the presence of titanium. Titanium, while not found in abundance in any one locality, must, nevertheless, be widely distributed for there appears to be more titanium than carbon in the earth's crust. The titanium oxides grade away in color from the white of TiO_2 through blue to purple when you get to Ti_7O_{12}. Attempts to make lower oxides with hydrogen were not successful. Ferric oxide at 1300° C. to 1350° C. dissociates into Fe_3O_4, or the lower oxide; and the oxides of iron or pure Fe or any compound of iron become FeO or, perhaps, Fe_3O_4 when fused with corundum. The bead, or boule, is light gray to colorless. Thus iron and titanium when fused with corundum undergo oxidation and reduction. The products that were obtained by this fusion were pinkish. In ordinary solutions, it is well known that every oxidation and reduction is accompanied by change in color. It was this phenomenon that was taking place in the production of the pinkish color. Attempts to get the blue were accompanied with so little success that substances other than iron were used to reduce the titanium. Anatase is blue and has a small percentage of one of the oxides of tin. SnO and SnO_2 with TiO_2 showed very little tendency of reduction. The reaction between iron and titanium is very strongly reversible. By simply adding a slight excess of one of the oxides, the reaction can be made to go in the direction of reduced titanium, resulting in perfectly blue corundum boule. The ultimate production of the sapphire in the laboratory left very few technical problems unexplained. This made it possible for the manufacturing department to take up work within a week after the successful conclusion of the research. Little change has been found possible since.

The corundum boule is in every respect identical with the earth-made product. Experts are much less able to tell the synthetic from the earth-made sapphire, than they are the synthetic ruby from the earth-made ruby.

After fusion only part of the iron and titanium oxides are left. Prof. Moses[8] found only traces of Fe_2O_3 and about 0.1 of 1 per cent of TiO_2. The analysis of the natural products extant before the synthesis of the sapphire did not show the presence of titanium oxide. Prof. Verneuil[9] has very carefully analyzed some sapphires from Australia, India and Montana that were perfectly clear under a magnifying glass with the following result in percentages:

Sapphire from	Australia.	India.	Montana.
Iron oxide	0.92	0.72	0.56
Titanium	0.031	0.04	0.058
Silica	a trace		0.10

The unpolished earth-made and the synthetic ruby or sapphire is far from being a thing of beauty It requires the lapidary's art to bring out their intrinsic qualities. The earth-made products can lend distinction to their wearers and therefore are very highly prized. The synthetic products because of their intrinsic beauty and genuine worth appeal to the many. About 10,000,000 carats of rubies and about 6,000,000 carats of sapphires are produced annually and the demand is growing very rapidly.

[6]Compt. rend., 66, 765 (1858).
[7]Gintl. Zeitschrift für angewandte Chemie, 1901, p. 1173.
[8]American Journal of Science, 30, 4th series, Oct., 1910.
[9]Compt. rend., 151, 1065, Dec. 5, 1910.

PHOSPHATE PRODUCTION LARGE.

Phosphate rock, which is the principal source of one of the three fertilizing elements necessary for plant growth, was marketed in the United States last year to the extent of 2,973,332 long tons, valued at $11,675,774. This was a slight decrease in both quantity and value compared with the figures for the preceding year, but the amount of phosphate rock mined was greater than in 1911, excepting in South Carolina. In Florida the increase was 3 per cent, in Tennessee it was over 12 per cent, and in the western phosphate field it was over 10 per cent.

Stocks of phosphate rock on hand also increased in the two main producing Southern States, Florida and Tennessee. On the whole the industry in the main southern phosphate field was active.

The production of phosphate rock in Florida was 81 per cent of the entire output of the United States. The output of this state, which at the present time leads in the phosphate industry, was with one exception, that of 1911, the greatest in the history of the state. The quantity marketed for the year was 2,406,899 long tons, valued at $9,461,297—a slight decline both in tonnage and value compared with 1911. Tennessee furnished 14.2 per cent of the phosphate marketed in the United States in 1912, the total production of the state being 423,331 long tons, valued at $1,640,476. In South Carolina 131,490 long tons was marketed, valued at $524,760—a considerable decline compared with 1911.

In the Western States the production of phosphate came from Idaho, Utah, and Wyoming and amounted to 11,612 long tons, a gain of 10.5 per cent compared with 1911. The value of the product increased considerably, the average price per ton being greater in 1912 than in 1911.

The United States Geological Survey has just published an advance chapter from "Mineral Resources, 1912," by W. C. Phalen, giving, besides statistics of production of phosphate rock for the whole country.

NATURAL AND SYNTHETIC RUBBER.*

By F. MOLLWO PERKIN.

Of late years the importance of rubber, or caoutchouc, has increased by leaps and bounds, partly owing to the enormous quantities which are employed in the manufacture of motor tires, and to the various other purposes to which rubber is now a necessary adjunct.

The trees and plants from which rubber is obtained only flourish in tropical and sub-tropical climates. A moist climate is required and a temperature with a minimum of 80° F. and a maximum of 108° F. The rubber zones where such conditions prevail are tropical America, the West Indies, tropical Africa, including Madagascar, Ceylon, and the Indian-Malay region, including Oceania.

The rubber-latex yielding plants are not always of the same species or botanical order. Furthermore, the quality and quantity of rubber yielded varies within wide limits even between the various species of the same order. In tropical America the rubber plants are mainly arborescent, although there are a few bushes and climbers. The African and Madacascar rubber plants are mainly climbers or vines. Latterly, however, trees which are indigenous to Africa have been found to be rubber-yielding. In the Indian-Malay region some of the trees such as *Ficus elastica* reach gigantic sizes, but there are also a number of species of climbers.

It is not within the scope of this paper to go into details as to the various species of the rubber plant or as to the methods of cultivation. A few words as to the methods of tapping the plants and obtaining and curing the rubber may, however, be of interest.

The present methods of obtaining the latex do not vary much from those employed by the natives who evolved them without scientific knowledge or training hundreds of years ago.

There is the wasteful method of felling the trees, which can only be justified under particular circumstances, as for thinning or clearing purposes in the opening out of virgin forests, or where, as sometimes happens, the trees are unable to bear incision without dying. It is well known that a vast amount of criminal waste has been carried on in past years by those who were in a hurry to grow rich and had no thought of the morrow. As the plants must be from five to six years old before they can be called rubber-yielding, obviously cutting down to obtain it is a suicidal policy, because even if the place were again immediately replanted no further supply of rubber would be available until another five years had passed. This is now being recognized, and the tendency is only to cut down for clearance purposes, and to sow or plant slips to form new rubber plantations.

Tapping is carried out by different methods in different regions. Probably the best methods are adopted in Brazil, where incisions are made with a special hatchet, the blade of which is little more than an inch wide, and as the cutting-edge of the axe is not much more than one-fifth of an inch deep, only the bark is incised and the wood of the tree is not injured. Before incising the tree the bark is well cleaned, and any rubbish removed from the foot of the tree. The cutting is either carried out in the early morning and the latex which exudes collected within a few hours of tapping, or the work is carried out in the night and the material collected in the morning. Little cups are placed below the incisions, and into these the white milky fluid drops. The quantity of fluid collected varies within wide limits, but is, on an average, about one ounce.

In Central America the incision is sometimes replaced by a small puncture. Within recent years a large number of special tapping instruments have been patented.

After the latex has been obtained from the trees, it is necessary to coagulate and preserve it. Although it will slowly coagulate of itself on exposure to the air and light, it is necessary to treat it to prevent putrefaction.

The latex by no means consists of pure india-rubber; generally speaking, not much more than about one-third of its weight is rubber, the rest being water, putrescible matter, small quantities of resinous material, etc.

A typical latex consists of:

Pure rubber	32 per cent
Albuminoid and mineral matter	12 per cent
Water	56 per cent

In this form the latex is a thin fluid, and, of course, could not be exported. In the process of coagulation the bulk of the water is removed, together with a large portion of the putrescible matter, and what remains should be sterilized in such a manner that it will not putrefy on keeping.

In order to coagulate Para latex, it is heated over a smoky fire, the process being as follows:

A bottomless earthenware vessel is filled with twigs and branches and a light applied. In order to create a draught the earthen furnace is raised from the ground by means of stones. As soon as a dense smoke makes its appearance, the native operator throws in palm nuts, then wood and nuts alternately until the jar is filled to within about 4 inches from the top. It is, however, only in the lower Amazon that the nuts are used, in other parts twigs and branches within easy reach are employed. When the smoke is sufficiently dense, the operator takes a wooden paddle which he exposes to the smoke for a few moments. He then smears the blade portion with water containing soft clay, to prevent adhesion of the rubber. After this treatment the end is dipped into the vessel containing the latex. The excess of latex is drained off, and then the mould is held flat side down about 2 inches above the mouth of the fire.

*From the Journal of the Royal Society of Arts.

By turning it over, both sides become equally smoked. There being only a film of latex on the instrument, the heat and smoke cause almost instant coagulation. The paddle is then again dipped into latex and the operation repeated time after time, until a large cake weighing about 10 lb. or 11 lb. is formed. It is then split down with a moistened knife and removed from the instrument.

It follows from the method of coagulating that the rubber gets thoroughly cured, since only thin films are acted upon during each operation. The coagulation is probably produced by the heat of the fire and by the products of partial combustion or distillation in the smoke; such, for example, as wood creosote and acetic acid. The *biscuits* so prepared require to be further dried, for which purpose they are placed in the branches of trees. The operation of drying takes several days.

Chemicad methods are largely employed; they consist in the addition of acids, such as sulphuric, hydrochloric, acetic, or citric acids, also of alum, mercury chloride, etc. One of the best seems to be a mixture of sulphuric acid and phenol. In using acids only very small quantities may be employed, otherwise the coagulation is upset. That is to say, there must only be sufficient acid added to coagulate the albumen present.

After rubber has been purified or cured in some way or other—and there are many processes which I have not time to discuss—it is sent to the market. Before, however, it is in a condition to be used for manufacturing purposes, it must go through a washing and rolling process.

Rubber, as it comes on the market, is rarely sufficiently pure for use without being first washed in order to free it from foreign matter, such as sand, pieces of bark, etc. There are four operations in the cleaning process: (1) Steeping in warm water to soften and clean it superficially; (2) slicing; (3) washing; (4) drying.

(1) When rubber arrives from abroad it is usually too hard to be conveniently worked. It is, therefore, placed in wooden vats containing water, which can be heated by steam. It remains in these vats from 12 to 24 hours.

(2) When it has been steeped long enough to make it sufficiently soft, it is removed and passed through the cutting machine, where it is shredded into fragments from 1½ inch to 2 inches square. The slicing can either be done mechanically or by hand.

(3) The rubber is then passed through rollers, generally corrugated, which revolve at different speeds, thus subjecting the rubber to a tearing and flattening process. As the rubber is being macerated water is caused to flow over the rollers. Any soluble impurities are thus dissolved and mechanical impurities, such as earthy material, twigs, bark, etc., washed away. The rubber is crushed and drawn out into a flattened sheet called crepe owing to its appearance.

Very considerable loss in weight occurs in the washing operation, as the following figures show*:

Para rubber	10-16 per cent
Peru sheets	30-40 per cent
Java rubber	20-35 per cent

(4) The final operation is drying. The washed rubber is sometimes spread on wire frames in a room heated by steam pipes. The room should be darkened, as the rubber must not be exposed to bright light when drying. The method most usually adopted at the present time, however, is to place the washed rubber in vacuum chambers which are steam-heated. The drying in this case is much more rapid.

After the rubber has been dried it is folded into bundles and stored in dry places away from the influence of light.

In some cases the rubber is washed and rolled at the plantations and is sent to the market as calendered sheets.

Vulcanization.—Undoubtedly the making of the rubber industry was the discovery of vulcanization. On heating to moderate temperatures, pure rubber becomes soft and tacky, whereas at low temperatures it turns hard and is rendered practically unworkable.

Vulcanization is not carried out to-day by dipping into molten sulphur, although in some cases the rubber is exposed to the action of sulphur vapor.

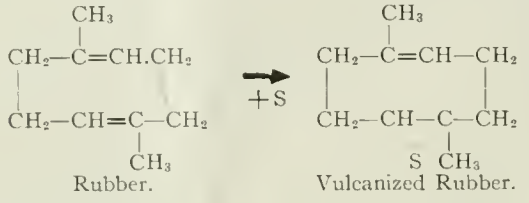
The usual process is to mix the rubber with sulphur and any filling material which is to be employed. This mixture is continually passed through rollers with the addition of oil or other solvent until an absolutely homogenous product is obtained. The filling materials employed are legion. For example: chalk, zinc oxide, antimony sulphide, lead oxide, powdered metals, silica, etc. The rubber containing the sulphur and filling material is employed for making the rubber articles before being vulcanized. Vulcanization only takes place at high temperatures. After the articles have been made they are placed in small or large chests, where they can be heated to the desired temperature under pressure.

The process of vulcanization requires great care and experience, as it is a very easy matter to spoil the goods by over-vulcanizing. Different rubbers, for example, require different periods of vulcanization, and rubber which has been "killed" by over-maceration in the washing process requires different treatment.

In the process of vulcanization as practically carried out, the average product only contains about 2.5% of sulphur. It is interesting to note, however, that quite different results are obtained by quick vulcanization at high temperatures with large excesses of sulphur, gradual vulcanization in which the temperature is slowly raised to a maximum, and by slow vulcanization at comparatively low temperatures.

And this is so, even if in every case the same degree of vulcanization is produced.

The chemistry of vulcanization is very complicated, and even although it has been practiced for more than half a century, very little is known as to what actually happens. Evidently, however, the sulphidation of rubber to cause vulcanization is one of addition, because sulphuretted hydrogen is not evolved in the process. As rubber contains unsaturated groupings, it is easy to understand how an addition product can be produced. Taking the simplest formula imaginable for rubber, we may suppose vulcanization to take place, thus:



Rubber. Vulcanized Rubber.

This formula would represent 23.5% of sulphur; if, however, the rubber molecule is multiplied by 10, so that it becomes

$C_{100}H_{160}$ instead of $C_{10}H_{16}$,

then the proportion of sulphur will be 2.35%. Now it has already been stated that in vulcanization practice on the average only 2.5% of sulphur is taken up. What the actual formula for rubber is we do not know at present, but undoubtedly it is very complex.

The final product in the vulcanization process is ebonite, the great value of which it is not necessary to go into here.

Gutta-Percha.—Before leaving the subject of natural rubber, I must just refer to one of the most valuable forms of rubber—gutta-percha. The time at my disposal, unfortunately, will only admit of a very short notice of this most interesting and valuable substance.

Gutta-percha appears to have been known of before the year 1656, since in a little book entitled "A Collection of Rarities," preserved at South Lambeth, near London, written by John Tradescant, mention is made that "the plyable Mazaer Wood, being warmed in water, will work to any form." How gutta-percha might be mistaken for wood will be readily recognized by an examination of gutta-percha as it is prepared by the natives.

Gutta-percha is similar in origin to india-rubber, being obtained from the later of the gutta-percha tree. The yield of gutta-percha, however, is very much smaller than is obtained from the india-rubber trees. The genuine gutta-percha trees do not appear to exist outside the Malay Archipelago, consequently these trees are much rarer than those which yield india-rubber. Unfortunately, owing to the wasteful manner in which the natives collect the gutta-percha, it is becoming more and more scarce. This is the more to be deplored, owing to the fact that attempts to form plantations of gutta-percha yielding trees have only been very partially successful.

In order to extract the latex from the trees, they are felled, and rings are cut in the bark about 2 feet apart, and running the entire length of the trunk. As a preliminary, after the trees have been felled, the branches are lopped off to prevent the latex running back into the smaller branches and twigs. Unfortunately, as a rule at least one-third of the latex remains in the trunk, and all of that which is in the leaves and branches. Instead of destroying the trees, processes for extracting the latex from the leaves have been invented. The dried leaves contain from 9% to 10% of gutta-percha, which can be extracted from them by means of toluene or other solvent.

On evaporating off the solvent the gutta-percha is left behind. By adoption of extraction processes the useful life of the tree is prolonged, and the total amount of gutta-percha obtained is greatly increased.

Chemically, gutta-percha would appear to be very similar to india-rubber, because when it is distilled it yields isoprene and other products similar to those yielded by india-rubber. Its physical behavior, however, is different.

Natural, that is unvulcanized, rubber when heated to about 100° C. softens and becomes more malleable, but it retains its elasticity. If it is compressed or stretched it returns to its original shape on removal of the force. On the other hand, when gutta-percha is treated in a similar manner it retains the shape given to it by the force. India-rubber, therefore, is elastic, and gutta-percha is plastic.

When rubber is exposed to air, particularly in bright light, it gradually loses its elasticity and becomes more or less viscous and tacky. On the other hand, gutta-percha under the some conditions becomes brittle and resinous.

The most important difference, however, is the behavior of the two substances towards sulphur. As we have already found, rubber vulcanizes and is vastly improved when heated with sulphur. But gutta-percha cannot be vulcanized. Luckily, however, its own intrinsic value renders it of the very greatest use in the pure state.

Owing to its high dielectric power, gutta-percha is of the utmost value for electrical purposes. Hundreds of thousands of miles of cable are insulated with gutta-percha, and for this reason alone the limiting of the source of supply would be a great catastrophe; unless, indeed, the advent of wireless telegraphy should do away with the necessity of employing cables.

Constitution of Rubber.—Rubber belongs to that excessively complex class of bodies known by the chemist as colloids. In chemistry, if we desire to ascertain the constitution of a body, we first endeavor to obtain it in a state of absolute purity, and to this

end various processes may be adopted. If a substance will dissolve in a liquid and afterwards come out in the form of crystals, it can usually be separated from other impurities which may occur along with it. For example, salt or sugar can be dissolved in water and afterwards obtained as pure crystals respectively of salt and sugar. Some solids, such as camphor, can be sublimed, that is, converted by heat into vapor and the vapor condensed against a cold surface, when a pure crystalline product is obtained, the impurities remaining behind. Liquids may be distilled, but colloidal substances cannot be purified by any of the usual methods, and even methods applicable to some colloids cannot be employed with rubber.

If rubber is strongly heated it can, indeed, be distilled, but the product which distils over is no longer rubber, but a mixture of certain liquids; the rubber is, in fact, decomposed. Rubber can be dissolved in certain solvents such as benzene and chloroform, but the solution of rubber in a solvent is different from that of other substances, although not of colloids. When the rubber is added to a so-called solvent it swells up owing to absorption of the solvent, and if sufficient solvent is employed, an homogeneous liquid is obtained, throughout which the rubber is evenly distributed. By the addition of a liquid such as alcohol to such a pseudo solution the rubber is precipitated out again, but its properties are considerably altered. It has not the same elasticity or nerve, nor does it vulcanize in the same manner as before.

For commercial purposes it is not actually necessary to know the constitution of rubber, its quality under various conditions being all that is required. Thus its distensibility or elasticity is important; that is to say, when stretched it should assume its original form immediately the force employed to stretch it is removed, it should vulcanize well, and so on. On the other hand, it is a matter of great importance to know the actual constitution of rubber in order to understand why it has its pecular properties, and if possible to arrive at some idea as to its formation.

As has been already mentioned, when rubber is subjected to distillation certain liquid bodies are obtained owing to the splitting up of the rubber. In 1860 Greville Williams examined this liquid and isolated from it a liquid called "isoprene," which boils at about 32° C. (89.6° F.). He also noticed that if this substance is kept for some time it changes its character, and from being a thin mobile liquid gradually becomes viscous. He further noticed that if this viscid product was distilled, then again isoprene distilled over, but a portion remained behind in the retort as a white spongy mass; also that when this spongy material was burnt it "exhales a peculiar odor, hitherto considered to be the characteristic of caoutchouc itself." In all probability, Greville Williams had actually produced synthetic rubber.

When isoprene is analyzed, it is found to consist of carbon and hydrogen in the same proportions as are obtained when pure rubber is analyzed, namely, 88.23% of carbon and 11.77% of hydrogen. The chemical formula for isoprene is written C_5H_8. If this formula is doubled we get $C_{10}H_{16}$, but it will be noticed that the percentage composition is the same, namely, carbon 88.23 and hydrogen 11.77. Now, as analysis of caoutchouc shows that it has the same percentage composition, it was early presumed that if isoprene could be caused to condense together rubber would result.

We have already seen that Greville Williams, by keeping it for some time, found it became viscid and thick.

In 1875, Bouchardet examined the products of distillation of rubber, and came to the conclusion that diisoprene $C_{10}H_{16}$, and other products obtained, were condensation products of isoprene, and showed that isoprene could be converted into a mixture of these substances.

In 1881 Hofmann, the renowned chemist, who was the first Professor of Chemistry at the Royal School of Mines, and a friend of the Prince Consort, found that methylbutadiene, which also has the same percentage formula as isoprene, and is what in chemistry we term an isomer of isoprene, condensed to form a viscous substance like rubber. When a substance condenses we call the process polymerisation. The first real proof of the polymerisation of isoprene to form rubber was by Sir William Tilden in 1882. In a note published in the *Chemical News* Tilden said : "Isoprene presents two characters which distinguish it from the two terpenes.* One is the peculiar explosive property of the white, syrupy substance which results from its oxidation by air.† The other peculiarity is its conversion into true india-rubber or caoutchouc when brought into contact with certain chemical reagents."

Two years later Tilden published a paper in which he showed that when turpentine is decomposed at high temperatures isoprene is produced. Now as caoutchouc can be produced from isoprene, and isoprene can be obtained from turpentine, it follows that if turpentine can be obtained in sufficient quantities and at a low enough price, and if the yield from turpentine is considerable, we have a possibility for manufacturing rubber on a commercial scale. Unfortunately, turpentine is not cheap, and turpentine is not plentiful; moreover, the yield of isoprene is small.:

Tilden found that polymerisation could take place by the action of hydrochloric acid.

Wallach later—1887—stated that isoprene is polymerised by the action of light, and forms a substance very like rubber in its properties. Wallach, in con-

*The terpenes also have the same percentage formula as isoprene.

†Greville Williams had also noticed this peculiarity.

nection with his brilliant and valuable researches on the terpenes, has this year been awarded the Davy Medal by the Royal Society.

In 1892 Tilden read a paper of remarkable interest, which did not then attract the notice which its importance warranted simply because rubber was so little understood, and was supposed to be a substance most undesirable for the chemist to study owing to its complexity. In fact, until recently, the chemist has almost always fought shy of resinous or gummy colloidal bodies. In this paper he remarked that the isoprene, a limpid liquid obtained from turpentine, had actually been converted into rubber simply by leaving it in bottles. Further, that the rubber so obtained agrees in all characteristics with Para rubber. It unites with sulphur in the same way as ordinary rubber, forming a tough elastic compound—that is to say, it can be vulcanized. About seven or eight years later Kondakow showed that other members of the isoprene or divinyl series could be polymerised into rubber-like bodies, either by exposure to light, or on keeping, or by means of chemical agents.

In 1906 Tilden showed samples of synthetic rubber before the British Association at York. These samples had been obtained by spontaneous polymerisation of isoprene. Up to this date may be said to be the first era in the production of synthetic rubber. The possibility of synthesizing rubber had been shown, and the product had, in fact, been prepared in small quantities.

It having been shown by Tilden, and confirmed by other workers, that isoprene on polymerisation formed rubber, the chief efforts of investigators in the first place were directed to obtain a satisfactory and cheap method for the preparation of isoprene.

The method employed by Tilden was to pass turpentine vapor through a red-hot iron tube containing turnings of the same metal. The yield of isoprene was, however, very small, other products being obtained at the same time.

Harries and Gottlob also employed turpentine and invented what they called the isoprene lamp. Turpentine was gently boiled in a flask in which was suspended a coil of thin platinum wire. An electric current was passed through the wire, which became white-hot. The mouth of the flask had a condenser fixed into it, through which water at about 50° C. was circulated. The turpentine vapor, as it came into contact with the heated wire, was converted into isoprene and other substances, which went off in the form of vapor. Now isoprene boils at about 36° C. The heavier boiling vapors were condensed in the warm condenser, and dropped back into the flask. The isoprene passed forward and was condensed.

Heinemann heated turpentine vapor to 500° C. in contact with silver or copper. However, turpentine was finally found not to be a satisfactory means of obtaining isoprene. Although a very large number of methods have been suggested, many of them are very complicated, the yields are poor and are extremely expensive. For these reasons, and also because the time at my disposal will not permit of it, I will only pick out a few of them.

Heinemann has also a process for obtaining isoprene by passing a mixture of acetylene, ethylene, and methyl chloride through a hot tube. The yield of isoprene, however, is very small, and the process is of no technical value.

W. H. Perkin, E. H. Strange, and F. E. Matthews also devised a rather complicated process, although it started from a cheap substance—lactic acid. They themselves, however, doubt whether complicated processes are likely to be of technical importance. The same authors have devised a method for preparing isoprene from amyl alcohol, to which I shall refer later.

In the various researches which have been made in connection with rubber, it has been found that other substances similar to isoprene can be polymerised to form rubber. Thus substances having conjugated carbon atoms arranged in the following manner will yield rubber-like products on polymerisation:

$$C{=}C{-}C{=}C.$$

Now, isoprene has this grouping, its formula being:

$$CH_2{=}C(CH_3){-}CH{=}CH_2$$

So also has butadiene, which is represented as follows:

$$CH_2{=}CH{-}CH{=}CH_2$$

We can formulate the condensation of two isoprene groups together to form rubber as follows:

$$CH_2{=}C(CH_3){-}CH{=}CH_2 \quad CH_2{=}CH{-}C(CH_3){=}CH_2 \longrightarrow CH_2{-}C(CH_3){=}CH{-}CH_2 \quad CH_2{-}CH{=}C(CH_3){-}CH_2$$

And of butadiene as:—

$$CH_2{=}CH{-}CH{=}CH_2 \quad CH_2{=}CH{-}CH{=}CH_2 \longrightarrow CH_2{-}CH{-}CH{-}CH_2 \quad CH_2{-}CH{=}CH{-}CH_2$$

It may be said, "but they cannot form the same rubber." The answer is that Harries has shown that Para rubber consists of at least three different substances. Numerous patents have been taken out for the preparation of butadiene and its homologues, amongst which may be mentioned that of Baeyer & Co., of Elberfeld, who obtain butadiene from phenol as the starting-point. That of Harries uses ethylmethyl ketone as raw material. The process of Baeyer & Co. consists in dropping hexaxylanol into an iron tube heated to 600°. Matthews, Perkin and Strange have produced butadiene from butyl alcohol.

I should like to draw attention to some of the difficulties which have to be overcome in dealing with the initial proposition of such a subject as the manufacture of synthetic rubber, and to illustrate this I will draw attention to the process I am most familiar with—that of the Synthetic Products Company, Ltd.

Fusel oil, from which isoprene can be prepared, is a product manufactured in considerable quantities,

and consists mainly of isoamyl alcohol. The crude oil was purified by fractional distillation, when the isoamyl alcohol was obtained:

$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!\diagdown\!\!\diagup CH.CH_2.CH_2OH$$

This was converted into the chloride by the action of hydrochloric acid. The next operation was to act upon it with chlorine gas, so as to convert it into the dichloride—

$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!\diagdown\!\!\diagup C\,Cl.CH_2.CH_2.Cl$$

The difficulty met with, however, was to obtain only the dichloride, the tendency being for the chlorine to react with the dichloride when formed to produce compounds containing still more chlorine, while a portion of the original product remained unacted upon. In order to get over the difficulty an apparatus was designed by Mr. Pim.

The isoamyl chloride is boiled in the flask until the chlorinating chamber is full of vapor and liquid drops fall from the end of the reflux condenser; a stream of dry chlorine is then passed in, but the isoamyl chloride must always be in excess, and this can readily be judged by noticing the color of the liquid as it drops from the condenser, because if the chlorine is passed in too quickly it will be of a yellow color. As quickly as the higher boiling dichloric is produced it drops back into the boiling flask, and as this is provided with a fractionating column, only the lower boiling isoamyl chloride can pass into the chlorinating chamber. By this means the dichlorides are removed from the further action of the chlorine. When the chlorination has proceeded far enough the product is submitted to fraction distillation with a fractionating column and separated into isoamylchloride and a mixture of dichlorides which distil at between 140° C. and 175° C. Three dichlorides are actually produced, but the chief one is the one already mentioned, viz., the 1:3 chloride.

All the chlorides when passed through a tube heated to 470° and filled with soda lime are converted into isoprene; consequently it is not necessary to separate them.

Now the only difficulty in obtaining isoprene by this method is the cost and the limited supply of the raw product amyl alcohol, the present price being about £140 per ton.

The same investigators, therefore, in conjunction with Professor Fernbach, devised a process for obtaining butyl alcohol cheaply, from which butadiene can be prepared. By the employment of a certain microbe it was found possible to ferment starch, and more lately sawdust, so as to obtain butyl alcohol and acetone. The butyl alcohol is chlorinated in a similar manner to the isoamyl alcohol, and by passing the dichloride so obtained over heated soda lime butadiene is obtained.

The processes involved may be presented as follows:

$$CH_3.CH_2.CH_2.CH_2OH$$
Butyl Alcohol.

Action of Hydrochloric Acid Gas—

$$CH_3.CH_2.CH_2.CH_2.Cl$$
Butyl Chloride.

Action of Chlorine—

$$CH_3.CHCl.CH_2.CH_2Cl$$
1:3 Butyl dichloride.

Splitting off hydrochloric acid by passing over heated soda lime,

$$CH_2{=}CH{-}CH{=}CH_2$$
Butadiene.

Butadiene is a gas at ordinary atmospheric temperatures, so it has to be condensed by means of a freezing mixture before it can be used to form rubber. The acetone produced along with the butyl alcohol is a valuable by-product, and it is of great value in the explosive and other industries. It follows, by the sale of the acetone, which it is claimed can be produced at a much lower cost than at present, the cost of butadiene is greatly reduced, and consequently that of the resulting rubber.

Quite recently Dr. F. E. Matthews, of the Synthetic Products Company, has devised a more simple and satisfactory method of preparing butadiene from butyl alcohol. The outline of the process is as follows, but I am not at liberty to give the actual working details.

The butyl alcohol is converted into *B*-butylene—

$$CH_3{-}CH{=}CH{-}CH_3$$

This is then chlorinated, when the dichloride is obtained—

$$CH_3.\overset{Cl}{\underset{|}{C}}H{-}\overset{Cl}{\underset{|}{C}}H{-}CH_3$$

By elimination of hydrochloride acid, and perhaps inter-molecular change, butadiene is produced. The yields in all the steps of the process are exceedingly good.

The badische Anilin und Soda-Fabrik in one of their processes use acetone as the starting product. The acetone is converted into pinacone, and, by splitting off water from the pinacone, 2:3 dimethylbutadiene is produced. The dimethylbutadiene being a derivative of butadiene polymerises to form a rubber-like product—

$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!\diagdown\!\!\diagup CO$$
$$\xrightarrow{\text{Reduction}}$$
$$\begin{matrix}CH_2\\CH_3\end{matrix}\!\!\diagdown\!\!\diagup CO$$

2 Molecule Acetone.

$$CH_3{-}\overset{CH_3}{\underset{|}{C}}{-}OH$$
$$\xrightarrow{\text{Dehydration}}$$
$$CH_3{-}\overset{CH_3}{\underset{|}{C}}{-}OH$$

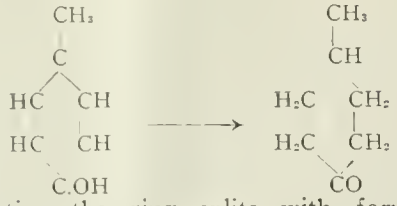
Pinacone.

$$CH_3{-}\overset{CH_2}{\underset{||}{C}}$$
$$CH_3{-}\overset{CH_2}{\underset{||}{C}}$$

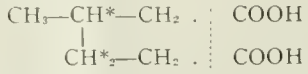
2:3 Dimethylbutadiene.

Fritz Hoffmann and Karl Coutelles of Baeyer & Co., Elberfeld, employed p. cresol as a starting prod-

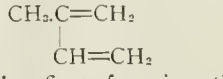
uct. The vapor is passed over reduced nickel, when the following reduction takes place:



On oxidation the ring splits with formation of β-methyladipic acid—



It will be noticed that, if the two COOH groups are eliminated and two hydrogen atoms, one from each of the parts marked with a star, isoprene will result.



This is carried out by first forming the ammonium salt, converting into the amide, and by the action of hydrochlorous acid into β-methyltetramethylendiamine:

and finally by exhaustive methylation isoprene is produced.

Another method of Baeyer & Co. is to start with L. β-dimethylorimethylenimine, but it has to go through five processes before isoprene is produced.

Heinemann worked out a process starting from starch, sugar or sawdust. From these products levulinic acid can be prepared. Levulinic acid is converted into methylthiophene, which on reduction yields isoprene. From two kilograms of starch 225 grams of rubber are said to be obtained.

So far I have referred to the production of the raw product from which the rubber is to be obtained. From my introductory remarks it will be clear that some process of polymerisation must be adopted. Thus exposure to bright light causes polymerisation. But, even on keeping for some time, or, as Tilden showed, by the action of strong acids, isoprene and its homologues are gradually converted into rubber. These processes, however, are hardly of commercial importance.

Apparently the first patent for the polymerisation of isoprene was taken out by Friedrich Baeyer & Co., of Elberfeld, in which it was claimed to produce synthetic rubber by heating isoprene to 200° C. for ten to twelve hours, when it is converted into a highly tenacious and elastic, but sticky mass. To remove the stickiness the product is treated with steam, and the material so obtained resembles natural rubber.

The chemists of the Elberfeld Farbenfabrik made the discovery that such substances as albumen, starch, blood serum, glycerine, etc., have the property of causing the polymerisation of hydrocarbons of the butadiene series.

In a recent patent the Elberfeld Fabrik make the following claims.

The polymerisation of the hydrocarbons (butadiene and its substitution products) may be promoted by carrying it out in the presence of any or all of the rubber-like products obtained in processes described in previous patents or in the presence of natural rubber. For example: (1) To 100 parts of the caoutchouc-like product obtained from butadiene by the action of sodium, but from which the sodium has been completely removed, 100 parts of butadiene liquified by cooling are added. The mixture is allowed to stand. After some time the polymerisation is quantitatively complete. (2) To 500 parts of the caoutchouc-like product obtained by polymerisation of isoprene in an incubator, by means of blood serum, 250 parts of isoprene are added. The mixture is kept at 30° C. to 40° C., and after a time is quantitatively polymerised to a caoutchouc-like product. (3) To 1,000 parts of the product obtained by polymerisation of $\beta\gamma$-dimethybutadiene, 1,000 parts of $\beta\gamma$-dimethylbutadiene are added. The mixture is heated in a closed vessel for four weeks to 70° C., when the caoutchouc-like substance is obtained. That is to say, having polymerised isoprene or its homologues by some particular means, the rubber so obtained can be employed to cause the polymerisation of further quantities of these hydrocarbons.

Prof. W. R. Hodgkinson has patented a method for producing rubber from isoprene by polymerising with sodamide or magnesium nitride.

One of the most interesting processes for polymerising isoprene, butadiene and their homologues was disvored by Dr. F. E. Matthews. In 1910 it occured to him to try the action of metallic sodium on isoprene. To this end a small piece of sodium was added to isoprene contained in a glass tube, which was then sealed. This was done in July, and then put on one side until the middle of August, when the contents had become viscid, a portion being converted into rubber. The tube was again set aside until September. The whole contents had by then been converted into straw-colored rubber. Further investigation showed that sodium was a general agent for polymerisation of this class of substance The condensation takes place much more rapidly at elevated temperatures. Metallic potassium is too rapid in its action and metallic calcium too slow. A patent for this process was applied for on October 25th, 1910. The beauty of this process lies in its simplicity, high temperature is not required, the presence of impurities does not markedly affect the action, and a comparatively small quantity of sodium only is necessary to cause the polymerisation of large quantities of isoprene or its homologues.

When the polymerisation is completed, the sodium can be removed by washing in alcohol in which it is soluble, whereas rubber is not.

When polymerisation takes place, a shrinkage of about one-third occurs in the liquid.

It is very interesting to note that Prof. Harries discovered this process quite independently, but when Messrs. Baeyer, with whom he collaborated, endeavored to take out a patent they found they had been forestalled.

The rubber so prepared has all the properties of natural rubber in regard to elasticity and the action of sulphur in vulcanisation. The vulcanisation, however, takes rather longer to complete. As has already been mentioned, natural rubber is always accompanied by small quantities of resinous and protein substances. The presence of these resinous bodies, although the amount is small, is supposed to aid in the vulcanisation. At any rate, rubber which has been freed from resins does not vulcanise so readily as when these are present. It has sometimes been stated that the presence of large quantities of resinous matter improves the rubber; this is, however, hardly borne out by experience, although a certain amount is an undoubted advantage.

Some time ago Harries prepared the ozonide of rubber, by acting upon dissolved rubber with ozone. In his research work Harries has found the formation of these ozonides of very great value in arriving at the constitution of substances. He now finds that the addition of a small quantity of the rubber ozonide very much increases the rapidity of polymerisation of isoprene or its derivatives.

Very many other methods for polymerising isoprene, butadiene, and their homologues have been suggested. For example, Ostromislensky, in a French patent, submits isoprene to the action of ultra-violet rays, cathode rays, Röntgen rays, or slow electric discharges. There is no doubt that these agents will cause polymerisation; but the action is not very rapid, and I imagine will be rather expensive, as my own experience in working with ultra-violet rays has shown that, as a rule, the efficiency is not high.

It has recently been stated that a Norwegian engineer has succeeded in producing rubber from turpentine. The artificial product is said to resemble natural rubber in every respect, and the difference in cost to be two-thirds in favor of the synthetic. It has already, however, been pointed out that turpentine is hardly likely to be a satisfactory raw product, owing to its high price, limited quantity and the fact that it is subject to commercial rings.

rubber substitutes, or materials partly consisting of

Rubber Substitutes.—It frequently happens that rubber, are referred to as synthetic rubber. This, of course, is not correct; either they are substitutes pure and simple, or they are merely impure rubbers.

For the manufacture of substitutes pure and simple very many different materials have been suggested. Thus unsaturated fatty oils, such as rape, linseed, castor, etc., are heated and subjected to a process of oxidation, or are mixed with sulphur and heated to high temperatures—in other words, vulcanized. Frequently also varying quantities of natural rubber are also added.

Substances of a gelatinous nature have also been suggested, which are then hardened with formaldehyde. In this category we have seaweed. The seaweed is boiled with ammonia, and then heated with oil and glutinous binding material and a vulcanizing substance.

In Amsterdam a factory has been erected to manufacture "synthetic rubber" from fish. The following details are obtained from the patent:

One hundred kilos of fresh or sea-water fish are extracted with water for two hours at a temperature of 90° C. to 100° C., and the extract filtered. The protein is then precipitated by means of acid. The precipitate is then filtered off and the solution rendered feebly alkaline with baryta water, the excess being removed by passing in carbonic acid. The mixture is again filtered, formaldehyde is added to the clear solution, and by evaporation in vacuum the elastic material is obtained.

According to a German analysis it would appear to consist of fish gelatine and natural rubber.

Another process, which is called a "process of manufacture of artificial indiarubber," is to immerse unvulcanized indiarubber in turpentine and mix until the whole of the turpentine is absorbed by the rubber. The mass is then kneaded with chloride of lime, and after going through a variety of other processes is called artificial rubber. Of course, this is not synthetic rubber, but merely treated natural rubber.

I have just mentioned the question of substitutes to draw attention to the difference between natural rubber, true synthetic rubber and surrogates.

At present there is room for both synthetic and natural rubber. Will there be in the future? And if there is not, which is going to push the other out?

USES OF INFUSORIAL EARTH.

The amount of infusorial or diatomaceous earth and tripoli produced in the United States in 1912, according to the United States Geological Survey, was valued at $125,466—$22,016 less than that of 1911.

Infusorial earth has been used largely as an abrasive in the form of polishing powders, scouring soaps, etc., and lately it has been found useful in the manufacture of dynamite as an absorber of nitroglycerine. It is also used as a packing material for safes, steam pipes, boilers, and as a fireproof material. In this country a new use for the material is reported in the manufacture of records for talking machines. In Europe, especially in Germany, infusorial earth has lately found extended application. It has been used in preparing artificial fertilizers, especially in the absorption of liquid manure, and in the manufacture of water glass, cements, glazing of tiles, artificial stone, paper, sealing wax, fireworks, gutta-percha objects, Swedish matches, etc.

SOME OBSERVATIONS ON THE FORMATION OF HYDROGEN SULPHIDE IN SEWAGE.*

Dr. ARTHUR LEDERER.†

When sewage undergoes anaërobic decomposition it releases hydrogen sulphide gas in varying quantities, often sufficiently large to be noted by its characteristic odor. The odor ordinarily found at sewage purification plants is probably due in most part to decomposition products other than hydrogen sulphide, such as ammonia, indol, skatol, phosphine, methyl merkaptan, phenol, phenylacetic-, phenylpropionic-, acetic-, butyric- and valerianic-acids and other compounds. In a general way we are aware that absence of air will favor the formation of these malodorous products of putrefaction, while in the presence of air decomposition may go on without any odor whatsoever, ammonia and hydrogen sulphide being at once oxidized to nitrates and sulphates.

Hydrogen sulphide may be produced from protein by purely chemical methods, such as fusion with caustic potash or by bacterial activity. In sewages the formation of the gas is largely due to bacterial action on the protein matter, this formation being similar to the formation of free ammonia, but the oxidation of hydrogen sulphide seems to depend much more upon chemical influence than in the case of ammonia.

The formation of hydrogen sulphide in sewages as derived from inorganic sulphates, first thoroughly studied by Beijerinck,[1] has been demonstrated on numerous occasions, to be altogether of bacterial origin. Sufficient data are not available as yet to form a definite opinion on the importance of the development of hydrogen sulphide from inorganic sulphates in sewage disposal plants. Recently Barr and Buchanan[2] reported large quantities of hydrogen sulphide in three sewage disposal plants, in which the sewage was very rich in sulphates. A specific organism, similar if not identical to the Spirillum desulphuricans of Beijerinck, has been isolated by these observers. H. W. Clark[3] observed the reduction of sulphates in sewages and so have a few others. A typical sulphate reduction also takes place in the "bialytic" tank (modified Dortmund tank) at the sewage testing station of the Sanitary District of Chicago, but no specific organism has been isolated as yet. Specific organisms taking part in the formation of hydrogen sulphide from sulphates were observed also by Zelinski,[4] Letts[5] and Van Delden.[6] Holschewnikoff[7] isolated a bacillus—the *bacterium sulphureum*—which was in his opinion a sulphate reducer. He claims to have found an increase in hydrogen sulphide on the addition of sulphates, but quantitative proof is lacking. He also obtained a strong hydrogen sulphide reaction on the addition of thiosulphates. However, this is a common property of many other bacteria.

Zelinski's description of the *bacterium hydrosulphureum ponticum* is interesting, inasmuch as he claims that the sulphates were decomposed under anaërobic conditions. Salkowski[8] in investigating the source of the development of hydrogen sulphide in urine states that it is possible that sulphates might be the source of its formation but certain conditions must exist, which he has not been able to elucidate. Huppert[9] admits that hydrogen sulphide can be formed at a fairly high temperature from sulphates in the presence of organic matter. Nadson[10] rather recently described a reduction of sulphates in the presence of peptone under anaërobic conditions employing pure cultures of proteus vulgaris. Hoppe-Seyler[11] ascribes the sulphate reducing property to methane in the status nascendi. Petri and Maassen[12] accepted nascent hydrogen as responsible for the reduction. Murray and Irwine[13] held that the reduction is due to the protoplasmic carbon of some micro-organisms, which first forms sulphides. The sulphides are acted upon by carbon dioxide and hydrogen sulphide is eventually formed.

There are a number of sewage purification plants in this country in which sulphate reduction has been noted, but little work has been done on the causes underlying this interesting phenomenon. It is safe to conclude that specific organisms fill a very important part in the process and that the formation of hydrogen sulphide from this source is to be clearly distinguished from the hydrogen sulphide accompanying putrefaction. For practical purposes it is immaterial from which source the hydrogen sulphide is being derived inasmuch as it draws impartially on the available oxygen of the stream into which it is discharged. The nuisance due to sulphate reduction is particularly apt to occur in sewages rich in mineral sulphates, such as iron sulphate derived from pickling liquors. In one case the total mineral sulphates in the crude sewage of the testing station in Chicago amounted to 23.2 p. p. m. of Sulphur (S), while the equivalent portions leaving the "biolytic" tank, in which sulphate reduction is marked, showed but 1.3 p. p. m. of S. On passing the effluent, which had the typical "rotten egg" odor, on to a sprinkling filter, the sulphates again increased to 7.6 p. p. m. of S. The filter was covered with a silk-like growth of beggiatoa, which are very rich in S granules and their oxidizing ability can be readily judged by the result spoken of. Similar results have been obtained on other oc-

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[1]Centr. Bakt. Parasitenk. 1895, Abt. II, vol. 1, p. 3.

[2]Iowa State College, Engineering Experiment Station, Bulletin 26.

[3]Report of the Massachusetts State Board of Health, 1903, p. 251.

[4]Proc. Russian Phys. Chem. Soc., vol. 25, (5) 1893.

[5]Proc. Roy. Soc. Edinburgh, March 4, 1901.

[6]Centr. Bakt. Parasitenk. 1903, Abt. II, vol. 11, p. 81.

[7]Fortschritte Med. vol. VII, 1889, p. 201.

[8]Berl. klin. Woch., 1888, p. 722.

[9]Neubauer and Vogel 8th Edition, p. 197.

[10]Handbuch der Technischen Mykologie, vol. 3, p. 126 (Omelianski's article).

[11]Z. physiol. Chem. 1886, vol. 10, 401.

[12]Arb. kais. Gesundh. 1893, vol. 8, p. 490.

[13]Trans. Roy. Soc. Edinburgh 1893, vol. 37, 496.

casions. The effluent of the sprinkling filter has been very rarely putrescible although the influent contained at times as much as 40 p. p. m. of hydrogen sulphide. The same sewage, which lost the greater part of the sulphates in the "biolytic" tank, showed only a slight reduction in the common, old style septic tank. The iron present has, of course, become combined with the generated hydrogen sulphide and the soluble sulphides so that there were but traces of iron left as a rule in the effluent of the "biolytic" tank, although at times for very short periods the sewage carried as much as 100 p. p. m. of iron (FE) and more. The precipitation of the iron salt by the hydrogen sulphide resulted in an effluent, which was particularly clear and low in colloidal matter but on storage free sulphur precipitated shortly. The active reduction process in the "biolytic" tank is accompanied by and perhaps stimulates the reduction of organic nitrogenous and carbonaceous matter, as borne out by the analytical data obtained. Altogether the observation points conclusively to specific bacterial action.

It seems of interest to investigate the rôle which some well known sewage bacteria and pathogenic bacteria might play in the reduction of sulphates in sewages or artificial sulphate media. Experiments along that line have in the past been extremely disappointing except in the very few cases in which it has been possible to isolate or identify a specific organism hitherto unknown. Fitz[1] cultivated a large number of bacteria without getting a trace of reduction on adding sulphates. Rubner[2] observed that bacterial cultures in bouillon or peptone bouillon may actually increase the quantity of sulphates. In some of his experiments the sulphates remained intact. In other cases the sulphates became diminished until they could not be determined but the decrease was not accompanied by the formation of hydrogen sulphide. The presence of sulphates did not seem necessary, however, when organic sulphur was present.

After experimenting with a large number of artificial media containing sulphur in the form of inorganic sulphates exclusively, I decided on a medium containing ammonium tartrate 10 gms., glucose 10 gms., basic potassium phosphate 1 gm., calcium chloride traces, sodium sulphate 10 gms. dissolved in 1 liter of water (medium "A"). Another medium employed (medium "B") had the same composition except that 50 mg. of glucose were added instead of 10 gms. It is claimed that if glucose is present in too large quantities, butyric acid fermentation may set in and the hydrogen sulphide reaction may be either absent or very much delayed. As a matter of fact there did not seem to be any noticeable difference in the sensitiveness of the reactions obtained with those two media during my experiments, but where one medium has been employed, "B" was the one resorted to. Some media, containing peptone in addition, have likewise been employed by me. They showed decided hydrogen sulphide formation on incubation with loopfuls of crude sewage, tank effluents, and sludges at either room temperature or at 37° C. This hydrogen sulphide formation is not the reaction of any specific organism, but the mass action of all bacteria preying upon the organic sulphur present in the peptone. Such decomposition is easily accomplished as will be noted later. The tests were qualitative only. However, the same amount of medium and the same size of loop were employed, so that a quantitative comparison of the results is justified. The hydrogen sulphide formation was observed in the first series of tests by inserting strips of filter paper, previously immersed in sterile lead acetate solution, into test tubes, the paper being fastened to the cotton plugs. A little glycerine was used in the preparation of the lead solution, so as to prevent the strips from becoming completely dried out on incubation.

The following cultures were used for incubating the various media: B. coli, B. typhosus, B. enteritidis, B. lactis, aërogenes, B. megatherium, B. mesentericus, B. cloacæ, Proteus vulgaris, B. acidi lactici, Proteus Zenkeri, Proteus mirabilis, B. mycoides, Sewage streptococcus, B. ochraceus, Strept. mitus, B. pyocyaneus, B. fluor, non-liquefaciens, B. choleræ suis, rose red coccus, B. prodigiosus, Staphyloc. pogenes albus, B. anthracis, B. dysentery and B. subtilis. One loopful of these cultures, grown on nutrient Agar, was inoculated into 10 cc. of the sterile media "A" and "B," containing sulphur in no other form but the inorganic. The cultures were incubated aërobically at 37° C.

Both media gave a negative result with every one of the species except B. cloacæ. B. cloacæ showed a slight but distinct quantity of hydrogen sulphide on the rim of the lead acetate paper, after four days incubation. The liquid showed a decided bacterial growth. B. pyocyaneus and B. fluor non-liquefaciens also gave a decided growth but no hydrogen sulphide. B. subtilis showed a distinct surface growth and likewise no hydrogen sulphide. A blank experiment was made in each case with sterile tap water as the medium. Chemical tests proved the absence of organic sulphur in the various ingredients employed in making media "A" and "B." Four strains of B. cloacæ were used at one time or another, but a positive hydrogen sulphide reaction has not always been obtained. Aërobic incubation gave 9 positive and 5 negative results on 3 to 10 days' exposure. Anaërobic incubation gave 4 positive and 3 negative results on 1 to 2 weeks' exposure. Thirty-seven degrees C. proved more favorable than 20° C. or room temperature. Whenever a reaction failed there was either no growth at all or very little growth noticeable. In positive cases, the longer the exposure the more distinct the reaction developed, but even in the most favorable cases the quantity could hardly be called anything but distinct traces as compared to the

[1]Chem. Berichte, vol. 12, p. 480.
[2]Arch. Hyg, vol. 16, p. 53.

amount of hydrogen sulphide generated by a culture of B. cloacæ in a 10 per cent peptone bouillon solution.

Quantitative investigation to prove an actual reduction of sulphates has not been undertaken. It is doubtful whether such an investigation would even prove successful, since there were never more than traces of hydrogen sulphide formed and unavoidable working errors might have resulted in differences possibly larger than the true differences. Inoculations of B. cloacæ into sterile tap water never resulted in hydrogen sulphide on incubation. I believe that the hydrogen sulphide formation in this case was not due to a sulphate reduction analogous to the reduction occurring with the Spirillum of Beijerinck, but rather that a small part of the mineral sulphate became converted into organic sulphur in the bacterial body, which on decomposition released hydrogen sulphide. It is very likely that some common forms of sewage bacteria take a part in the formation of hydrogen sulphide from the mineral sulphates under specific conditions, which have as yet not been reproduced artificially.

Where the reduction is as marked as in the "biolytic" tank, spoken of before, there can be hardly any doubt of specific action. When I incubated medium "B" under aërobic conditions with a loopful of the sludge from that particular tank, I obtained in a few hours a decided hydrogen sulphide reaction on lead acetate paper. The sludges from two other septic tanks gave a weak reaction in the same period and the sludge from a plain settling tank showed no reaction at all. When the incubation was extended from one day or longer all sludges showed a strong hydrogen sulphide reaction. The sludge from the "biolytic" tank, incubated under anaërobic conditions also gave a distinct reaction in medium "B."

It is also interesting to note that a number of the common sewage bacteria largely retard the oxidation of the black iron sulphide in sewage sludge. Test tubes containing a sterile medium consisting of 10 per cent sludge in sewage were inoculated with loops of B. coli, B. typhosus, B. enteritidis, B. megatherium, B. mesentericus, B. cloacæ, Proteus vulgaris, Proteus Zenkeri, Proteus mirabilis, B. mycoides, B. pyocyaneus, B. fluor, non-liquefaciens, Staphyloc. pyogenes, albus and B. subtilis. The tubes were incubated aërobically at 37° C. Soon the blank, containing the sterile medium began to change. The black iron sulphide gradually became converted into brown basic sulphate from the top downward. In one week all of the black color had disappeared. The B. cloacæ, B. pyocyaneus, B. fluor, non-liquefaciens tubes, after that time, still showed the black color throughout, but the B. cloacæ sludge began to show signs of oxidation on the surface. Other species showed this effect to a much lesser degree. With some species, as B. megatherium and B. mesentericus, the oxidation proceeded nearly as quickly as in the blank sludge. One cc. of sewage, one loopful of river mud, sludge from the "biolytic" tank, septic tank and settling tank added to test tubes containing the medium prevented the oxidation of the sludge as long as they were under observation (ten days). However, 1 cc. of fresh lake water added to the sterile medium quickly changed the black color into brown. As a matter of fact, the lower tube was completely oxidized. Werigo[14] incubated oxidized sterilized mud from the coast of the Black Sea with small amounts of non-sterilized black mud. The gray color of the oxidized material quickly changed to its original black. The black color was due to the presence of iron sulphide. Philippowitsch[15] and Brussilowsky[16] observed that the blackening of that particular sterilized mud took place on incubation with the water from the coast and even river water. They did not consider this reduction process as due to specific bacteria. B. phophorescens and B. typhosus likewise gave a black color in the mud on inoculation.

The question arises as to whether in a sewage purification plant an effluent in which an active sulphate reduction takes place should be looked upon as more putrescible simply because it contains more hydrogen sulphide or not. The old Hamburg putrescibility test, which consisted of the determination of the organic sulphur in the sewage effluents, did not take the inorganic sulphate reduction into account. Possibly the formation of hydrogen sulphide from sulphates is more general than is supposed. I believe a distinct mistake would be made if the sulphates are disregarded. Fortunately Spitta and Welder's methylenblue test permits the normal and abnormal biological processes to proceed on a small scale. The reducing compounds, formed, react no matter what their source may have been. The Hamburg putrescibility test assumed that organic sulphur is the main source of the putrescent decomposition products. Under ordinary conditions, the hydrogen sulphide, released during the putrefactive process in a sewage purification plant, is hardly noticeable and can be detected in the majority of cases only by sensitive chemical tests. Yet its development is general and proceeds continuously, just as does the conversion of highly complex nitrogenous matter into free ammonia.

That organic sulphur in protein bodies constitutes a source of hydrogen sulphide gas has been known for a long time. Petri and Maassen[17] observed this phenomenon with the B. erysipelatus suis. The work was originally undertaken by these authors with the view to establish, if possible, the relation between the formation of hydrogen sulphide and hog erysipelas, but it has since been found that practically all known bacteria form hydrogen sulphide from protein compounds under certain conditions. The ability to form hydrogen sulphide will largely depend upon the amount of organic sulphur present. The authors men-

[14] Congress internat. d'hydroth. et de climat. Biarritz 1886.
[15] Wratch 1887, No. 16.
[16] Wratch 1890, p. 717.

tioned employed a large number of species, most of which were pathogenic to animals. All of the species formed hydrogen sulphide. Rubner[18] also took a large number of cultures and inoculated them into extracts from the thymus, lung, liver and spleen, from which the inorganic sulphur had been removed. Hydrogen sulphide has been obtained whenever the growth was strong. Thus, he proved that the sulphates were not necessary for the formation of the gas. He disagreed with Petri and Maassen on the cause for the hydrogen sulphide development. Rubner concluded that the formation of hydrogen sulphide is not a secondary reduction process, due to the formation of nascent hydrogen, contrary to the belief expressed by the other two authors. Stagnitta—Balistreri[19] on working with twenty-three various species of bacteria, found that forty per cent of them gave hydrogen sulphide in peptone bouillon and plain bouillon. He tried to obtain some quantitative data by comparing the extent of the color on lead acetate paper to the color of the papers exposed to known quantities of hydrogen sulphide. Petri and Maassen found that the addition of sulphates and thiosulphates will also result in the development of hydrogen sulphide. With regard to the thiosulphates this has also been observed by Rosenheim and Gutzmann.[20]

It has been stated that bacteria can not be classified as hydrogen sulphide formers and non-hydrogen sulphide formers, as was first supposed. On addition of 10 per cent peptone bouillon to ten species, which had not reacted in bouillon containing less peptone, Petri and Maassen obtained a strong hydrogen sulphide reaction.

I undertook to incubate the species, employed during my work, previously mentioned, in media containing sulphur in various forms and found in a general way that the results coincided with the results of former observers. A medium of the same composition as medium "A" but containing sodium thiosulphate instead of sodium sulphate gave more or less hydrogen sulphide in each case on aërobic incubation at 37° C. In a few cases the quantities were so small as to be hardly perceptible on lead acetate paper. Sulphur added to sterile sewage formed hydrogen sulphide aërobically with all species except B. lactis aërogenes, Proteus Zenkeri, Proteus mirabilis, B. pyocyaneus, Staphyloc. pyogenes albus, B. anthracis, B. dysentery and B. subtilis. It is very likely that the number of positive tests would have been greater if more time had been allowed for incubation. Plain bouillon gave a decided reaction only with B. enteritidis, Proteus vulgaris and traces with B. mesentericus. The rest proved negative on aërobic incubation for over one week. Lactose bouillon gave a strong growth with B. enteritidis and Proteus vulgaris. A few species showed traces of hydrogen sulphide in bouillon containing 10 per cent peptone (reaction + 1). All cultures gave a hydrogen sulphide reaction sooner or later on aërobic as well as anaërobic incubation.

On repeating the experiments with 10 per cent peptone bouillon several times, it was interesting to note that the strong hydrogen sulphide formers gave a strong reaction throughout the entire series, while species giving weak reaction would on repetition always prove weak in the same length of time.

I am not inclined to attach very much significance to this quantitative difference in the behavior of the bacteria towards the organic sulphur in peptone though it might prove valuable to classify the various species distinctly as to their hydrogen sulphide forming properties. This can be done, providing certain standards are adopted for time of incubation, the uniform composition and reaction of medium, temperature of incubation, age of culture, etc. The virility of the culture is a factor of great importance. A rejuvenated culture will show hydrogen sulphide sooner than an old stock culture. Care was taken, therefore, to employ fresh cultures throughout the tests.

In order to gain some information on the hydrogen sulphide forming properties of crude sewages in such a peptone medium a few quantitative experiments were made, which are given in the following:

A 10 per cent peptone bouillon was prepared and 1 cc. of an approximate 10 per cent sodium sulphate solution was added to each test tube to allow for a possible sulphate reduction. The quantity of medium in each test tube was exactly 15 cc. A quantitative determination showed that the test tube contained 12.0 mg. of organic sulphur and 86.9 mg. of sodium sulphate anhydrous. Each test tube was provided with a tight fitting rubber stopper. The upper part of the thistle tube with a double bend fitted into the stopper and some absorbent cotton moistened with a saturated solution of basic lead acetate with 5 per cent of glycerine was plugged into the funnel, so that all hydrogen sulphide formed would be bound chemically. One cc. of crude sewage was added to the medium and the mixture incubated aërobically as well as anaërobically at 37° C. for exactly twenty-four hours. The test tube was then put into warm water to drive out any gaseous hydrogen sulphide in solution. The cotton plug and the incubated liquid were washed into an Erlenmeyer flask and the liquid acidified with sulphuric acid in order to release the hydrogen sulphide bound in the form of sulphides. The liquid was then distilled and the distillate received in a N/100 silver nitrate solution. The distillate was made up to 100 cc. thoroughly shaken, filtered and 50 cc. of the filtrate titrated with N/100 potassium sulpho-cyanate solution, using ammonio-ferric-sulphate solution as an indicator.

Two tubes containing the sterile medium were incubated and served as blank tests. There is always some hydrogen sulphide split off even from a 10 per cent peptone solution on mere boiling. It is, therefore, ab-

[18] Arb. kais. Gesundh. 1893, vol. 8, p. 318.
[19] Arch. Hyg. vol. 16, p. 53.
[19] Arch. Hyg. vol. 16, p. 10.
[20] Fortschritte Med. 1887, No. 11.

solutely necessary to run blank tests. The average of the blank tests showed that 15 cc. of the sterile medium distilled with the acid under the same conditions as the inoculated cultures gave about 0.33 mg. of hydrogen sulphide. The sterile medium incubated for 24 hours and then distilled as before gave on an average 0.39 mg. of hydrogen sulphide or an excess of 0.06 mg. over the direct distillation. The figures remained the same for aërobic as well as anaërobic incubations. The hydrogen sulphide figures in Table I represent the gas with the blank subtracted. Very good checks have been obtained in each case for the blanks as well as for the inoculated media.

TABLE I.

Sewage Ser. No.	Total suspended matter p. p. m. (sewage).	Oxygen consumed p. p. m. (sewage).	N as free ammonia p. p. m. (sewage).	N as organic nitrogen p. p. m. (sewage).	Relative stability. (sewage).	H_2S developed aërobic mg. (medium).	H_2S developed anaërobic m. g. (medium).
1..	296	60	5.6	6.9	29*	0.95	0.95
2..	134	59	8.8	9.6	26*	1.04	1.08
3..	88	24	6.4	8.8	53*	0.77	0.91
4..	106	..	8.4	6.8	56*	0.67	0.90
5..	90	28	8.8	8.0	64*	1.06	1.13
6..	142	56	5.6	9.3	29†	1.01	1.05
7..	106	58	8.4	8.1	29‡	0.94	0.91

*Dilution: 1 sewage to 3 lake water.
†Dilution: 1 sewage to 4 lake water.
‡On incubation for twenty-four hours at 37° C in 10% peptone bouillon containing sodium sulphate.

The results indicate that under anaërobic conditions, the quantity of hydrogen sulphide formed is somewhat larger, particularly in sewage No. 4. Apparently the other data obtained do not bear a distinct or definite relationship to the amount of hydrogen sulphide developed. This is to be expected since we know that the formation of hydrogen sulphide in sewages or in proper artificial organic solutions is a specific property of the bacterial cell body. The action is selective and depends apparently a great deal upon the position of the sulphur radicles in the protein molecule of which we know little. A bacillus may be a strong nitrate reducer and yet a very wea hydrogen sulphide former, although both processes are reduction processes.

The subject of putrid odors in sewages is a highly complicated one. I have spoken of one phase only, viz: the formation of hydrogen sulphide in its relation to inorganic or organic sulphur compounds, but we must also consider that other organic volatile sulphur compounds are likely to be formed, which from a practical working standpoint might prove troublesome.

The writer wishes to express his appreciation of the valuable continuous assistance of Mr. Frank Bachmann, assistant chemist of the Sanitary District, in the work necessary for the preparation of this paper.

Turpentine, which was quoted in Hamburg at $15.23 to $15.47 per 220 lbs. on Jan. 1, and $14.40 on March 19, had reached a level of $13.56 for prompt delivery on July 10.

NEW ELECTRIC STEEL WORKS IN ENGLAND.*

The new electric steel plant being established on the south side of the Tyne, immediately opposite the Elswick shipyard and ordnance department, by the Stobie Steel Co. will be ready for operation in September.

These works will at the outset comprise a melting shop 250 feet long by 60 feet wide and 50 feet high, with a lower bay 26 feet wide extending along one side of the main building. The installation includes one 15-ton electric steel furnace working on three-phase current, one 15-ton furnace operating on two-phase current, and one 3-hundredweight ferroalloy furnace, single phase. The furnaces designed and erected by Mr. Victor Stobie, of Sheffield, will be worked from a steel platform measuring 80 feet by 28 feet and placed 8 feet from floor level. The buildings include, in addition to the usual general and private offices, laboratories for steel testing and micrographic research.

Three-phase current at 40 periods, 6,000 volts, will be obtained from the Newcastle-on-Tyne Electrical Supply Co., and will be stepped down from 6,000 volts to about 65 volts. The supply cables will be duplicated from the Dunston power station, and continuity of supply will be further assured by a system of interconnections between the large current consumers in the Tyneside district. The furnaces will be tilted electrically for emptying and the regulation of the supply of electricity to the furnaces will be automatic. The switch house is a two-story brick and ferroconcrete building 25 feet square, and it contains 11 panels of high-tension feed and switch gear. Two transformers, to supply a crane, some auxiliary motors, and lighting, are also placed in the switch house.

A river jetty capable of accommodating seagoing vessels is directly connected to the private sidings, and an electric crane will handle the material from ship to wagon. The sidings will also be connected with the North-Eastern Railway system, and all shunting on the works siding will be performed by a 200-horsepower electric locomotive. Pig iron, scrap, and other heavy raw materials will be delivered to a siding which extends 60 feet down the center of the main building, and an electromagnet attached to the overhead crane will unload the trucks. A 20-ton weight bridge for dealing with truck loads, and also ladles of molten metal, is placed under the crane track, and a 3-hundredweight electrically driven power hammer is provided for testing samples of the steel whilst the main body is still molten in the furnace. This hammer will also be used for forging the various furnace steels, and a blacksmith's shop and an installation of machine tools will complete the mechanical testing plant.

*London Times Engineering Supplement.

METHODS OF ANALYSIS USED IN THE LABORATORIES OF THE ARMOUR INSTITUTE OF TECHNOLOGY.

Methods of Analysis Used in Analysis of Milk and Milk Products.

(CONCLUDED.)

Determination of the Casein in Milk by Means of the Refractometer:* Fifty c.c. of fresh milk are diluted to 250 c.c. with distilled water and 75 c.c. of tenth normal solution of acetic acid added, the mixture being continuously and rapidly stirred throughout the addition. The precipitate is allowed to settle and the supernatant liquid poured through a 15 c.m. S. & S. No. 589 "white band" paper. The precipitate is then washed by decantation with distilled water several times, the washings, and subsequently the precipitate being transferred to the filter paper. Filter and precipitate are allowed to drain for about an hour and then transferred to a dry beaker and 100 c.c. of tenth normal NaOH solutions added, when the paper is macerated thoroughly by means of a rubber tipped glass rod until the precipitated casein is completely dissolved. The mixture is then filtered and its index of refraction taken, the temperature being as near as possible to 20 deg. C.

The index of refraction of the mixture (n) minus the index of refraction of the NaOH solution (1.33444) gives the index of the casein solution, and this value divided by a constant gives the weight of casein in 50 c.c. of milk.

$$\text{weight of casein} = \frac{n - 1.33444}{0.00152}$$

ANALYSIS OF CONDENSED MILK.

Owing to the high concentration of this product, it is more convenient to work with a diluted sample. To this end, 40 grams are weighed out, diluted with 50 c.c. of water and the whole washed into a 100 c.c. measured flask and diluted to the mark with water.

1. Determination of total solids and ash. Ten c.c. of the above diluted sample are diluted with exactly 10 c.c. of water. Five c.c. of this solution, equivalent to 1 gm. of original sample, are taken, total solids and ash being determined exactly as in the case of milk.

Proteids are determined exactly as in milk.

Lactose is determined exactly as in milk, using 5 c.c. of the 40% solution, diluter to 40 c.c.

Fat is determined as follows:

Fifteen c.c. of the 40% solution is placed in a Babcock test bottle, diluted almost to the neck of the bottle, 4 c.c. of Fehling's copper solution added and the whole centrifuged.

This separates the fat and proteids as a precipitate at the bottom. The clear supernantant liquor is withdrawn with a pipette, and the precipitate washed twice by shaking with water, centrifuging and withdrawing the water. Finally water is added to about 17.5 c.c., 17.5 c.c. of sulphuric acid introduced, and the test completed as in the Babcock determination upon milk. The reading multiplied by 3 gives the per cent of fat in the original sample.

Lacking a Babcock tester, fat may be determined by the paper coil method described for milk, about 5 grams of the diluted solution as used for total solids being absorbed in a paper roll, and the determination completed as usual.

Sucrose: This is determined by difference:

Total solids — (lactose + proteids + fat + ash) = Sucrose.

ANALYSIS OF BUTTER.

Determination of moisture:

(1) A sample of about 2 grams is weighed into a flat bottomed aluminum milk dish and heated at 100° (preferably in a water-jacketed air bath) to constant weight. Loss of weight is moisture. Reserve the dry sample further for fat.

(2) A five gram sample is placed in a large platinum dish, melted carefully over a free flame, and finally heated cautiously until no moisture condenses upon a cool mirror held over the dish. Loss in weight is moisture.

Determination of fat: The dried sample from the moisture determination is washed from the dish into a small beaker with petroleum ether, filtered upon a weighed Gooch crucible, and thoroughly washed with petroleum ether, the filtrate and washings being caught in a small tared flask. The solvent is evaporated from the filtrate, the residual fat dried for an hour at 100° and the whole weighed. Difference in weight gives total fat. The insoluble portion on the Gooch is dried to constant weight. This gives the sum of the casin, ash and salt. This residue is then ignited gently over the flame, the temperature being finally raised to just below red heat. The loss in weight represents casein, the weight of the residue, mineral matter.

Determination of Salt.—Ten grams of butter are weighed into a small beaker and transferred by means of hot water into a separatory funnel (100 c.c.). Here it is shaken with hot water, allowed to stand until

*Robertson, Jour. Ind. & Eng. Chem. 1., 723 (1909).

separation takes place, the water drawn off into a 250 c.c. measured flask and the operation twice repeated with fresh water. The flask is filled to the mark and 50 c.c. portions (representing 2 grams of the original sample) are titrated with N/10 silver nitrate solution, K_2CrO_4 solution being used as an indicator. If desired, a 50 c.c. portion may be just acidified with nitric acid, silver nitrate solution added in slight excess, the whole boiled until the supernatant liquid is clear and the silver chloride filtered on a weighed Gooch, washed free from soluble silver, dried at 130° and weighed as AgCl, from which NaCl is calculated.

The examination of butter is not complete without a determination of the volatile fatty acids (Reichert Meisel Number), for it is through this that adulteration by foreign fats is best detected.

The Reichert Meisel Number is the number of c.c. of N/10 Ba $(OH)_2$ required to neutralize the volatile fatty acids from 5 grams of sample.

DETERMINATION.

Special solutions required:

1. KOH, 100 grams per 58 c.c. of hot water.
2. H_2SO_4, 200 c.c. diluted to 1 liter.
3. Ba $(OH)_2$ solution, standard and of approximately tenth normal strength.

A sample of butter is melted at 60° C. and dried at that temperature until the fat is completely separated from water, curd and mineral matter, when the whole is filtered through a dry paper in a hot water funnel.

A sample of approximately 5 grams is weighed into a round bottomed flask made of thick, well annealed glass and provided with a stopper which may be clamped and held air tight against pressure from within.

To the sample in the flask 2 c.c. of the strong KOH solution are added, and the whole treated for one hour in a boiling water bath, the contents of the flask being carefully rotated from time to time during the saponification period.

When saponification is complete, the flask is allowed to cool and opened. The soap is dissolved in 132 c.c. of recently boiled water, warmed on the water bath until the solution is clear and cooled to 60° C. A few pieces of pumice stone are thrown in, and then 8 c.c. of the diluted sulphuric acid added, the flask stoppered once more as in saponification and heated in boiling water until the fatty acids appear as a clear layer on top of the aqueous solution. This will probably take several hours. The solution is cooled to room temperature to avoid loss of volatile fatty acids, opened and connected by means of a distilling bulb with a glass condenser and distilled at such a rate as to collect exactly 110 c.c. of distillate in as near 30 minutes as possible.

The distillate is mixed, filtered through a dry filter and exactly 100 c.c. of it titrated with the standard barium hydroxide solution.

The volume of tenth normal alkali solution is increased by one-tenth of the number of c.c. used, this number divided by the weight of sample and multiplied by 5 to give the Reichert Meisel Number.

EXAMINATION OF CHEESE.

The sample is prepared for analysis by cutting or shaving very fine and mixing thoroughly, the sample being kept in a well stoppered jar.

Moisture, ash, fat and casein are usually determined.

Moisture and Ash.—A 2.5 gm. sample is weighed into a tared platinum dish provided with a mat of ignited asbestos to absorb the fat which melts out of the cheese. The whole is heated to constant weight at 100° C., loss in weight being moisture.

The residue from this determination is heated carefully over a low flame and finally reduced to ash in a muffle at a low red heat, the weight of residue being ash.

Proteid.—This determination is carried on exactly as described under the subject of milk, a 2 gm. sample being used.

EXAMINATION OF ICE CREAM.

It is advisable that the analyst have a sample of ice cream in the frozen condition rather than one that has been allowed to melt. Melted ice cream sours very readily and if the sample is sour, a separation takes place which makes it impossible to get a true average sample, and in consequence, a true determination of the fat.

If the sample comes in the melted condition it should be immediately preserved by the addition of either a few drops of formaldehyde or a pinch of sodium benzoate.

The Determination of Fat.—A sample of nine grams of ice cream is weighed into a Babcock test bottle and to it 10 c.c. of glacial acetic acid (99.5 per cent) added. The bottle is shaken and placed on the water bath and concentrated sulphuric acid added dropwise from time to time, the whole being frequently shaken and allowed to digest on the water bath for several minutes after each addition of acid. When all lumps are broken up and the solution assumes a chocolate-brown color, the determination is finished exactly as the determination of fat in milk by the Babcock method. The direct reading of fat multiplied by 2 gives the per cent of fat in the ice cream.

Note.—If it is necessary to identify the fat of ice cream, a sufficient quantity of the cream is treated exactly as the sample is treated for the separation of fat for its determination as described above, except that a long digestion on the water bath will separate the fat if a large centrifuge is not at hand. The fat so obtained is melted, filtered and its refractive index, and, if necessary, its Reichert Meisel Number determined.

Detection of Thickeners.—Gum tragacanth and, occasionally, agar agar are added to ice cream to give it the appearance of richness. The presence of these thickeners is detected as follows: 50 c. c. of melted sample (which should not be sour) are diluted

with 25 c.c. of water and the whole boiled to assure the solution of any thickener, when 2 c.c. of 10 per cent acetic acid is added, the solution boiled and three heaping teaspoonfuls of kieselghur added, the mixture shaken and promptly filtered through a folded paper. To 3 c.c. of filtrate 12 c.c. of 95 per cent alcohol are added and the mixture shaken. This precipitates milk proteins, the gums and possibly gelatin if the latter were present in large amount. To this are added 3 c.c. of a mixture of 95 c.c. of 95 per cent alcohol and 5 c.c. of concentrated hydrochloric acid. The milk proteins are soluble in this acid alcohol and a clear solution at this point proves the absence of gums or other vegetable thickeners. If a mere turbidity appears, thickeners are probably not present, as this turbidity may be due to the presence of egg in the material. Three c.c. of water added to the test should dissolve anything but the thickeners. If the precipitate is stringy and cohesive, gum tragacanth is indicated; if flocculent, agar agar or other vegetable thickeners.

Howard's Test for Gums.—Ten c.c. of melted sample are precipitated with acetone and washed by decantation with 2 or 3 portions of alcohol, the centrifuge being used. The washed residue is boiled with 6 to 8 c.c. of water and 1 c.c. of 10 per cent sodium hydroxide solution for half a minute, and after cooling for a few minutes, filtered. The clear filtrate is heated to boiling and to it one and one-half volumes of warm alcohol added, the whole being shaken. A flocculent precipitate indicates the presence of gum tragacanth or agar agar. A slight turbidity should be disregarded.

Detection of Gelatin.—Reagents required: (1) An acid solution of mercuric nitrate prepared as follows: A weighed quantity of mercury is dissolved in twice its weight of concentrated nitric acid (sp. gr. 1.42) and the solution diluted with 25 volumes of water. (2) A saturated aqueous solution of picric acid.

The test is carried out as follows: To about 10 c.c. of the melted sample is added an equal bulk of the mercuric nitrate solution and 20 c.c. of cold water, the mixture shaken and, after a few minutes, filtered. If much gelatin is present the filtrate will be opalescent; if absent or in small quantity, it will be perfectly clear. To this solution is added a few drops of the picric acid solution. A yellow precipitate shows the presence of gelatin. The test is of such delicacy that a cloudiness is produced by one part of gelatin to 10,000 parts of milk or cream.

Detection of Starch.—This substance is detected by the familiar iodo-starch reaction, as follows: A few c.c. of the material is diluted with warm water and to it added a few drops of a solution of iodine in aqueous potassium iodide. A strong, dark blue color indicates the presence of starch.

Bacterial Count.—A sample of fresh material is treated exactly as in the case of milk, except that it is well to have a dilution that corresponds to one part of sample to 5,000 of water.

INVESTIGATION OF SOAP POWDERS.

By G. A. BRAGG.

The work reported in this paper was done by the writer during 1912 in the State Water Survey Laboratory at the University of Kansas, under the supervision of Mr. C. C. Young, director. The object of the work was to secure comparative data on the composition of as large a number as possible, of the more common soap powders, washing and scrubbing compounds, and polishers. These have all been designated by the general title of soap powders, for the reason that of the twenty-one mixtures analyzed, all but one contained soap, and all but two were in powdered form.

All of the samples used for analysis were collected by state food inspectors, from grocery and supply houses in different parts of the state where they were being offered for sale. Each package was sealed by the inspector at the time of purchase and was not opened until the analysis was begun in the laboratory, at which time a sample, usually about one-fourth of a package, was placed in a dry glass stoppered bottle to prevent any change in the moisture content after analysis was begun. The atmosphere of the laboratory was drier than that of the average grocery store, and any moisture absorbed by the powders before they were bottled up for analysis would hardly be as much as would have been absorbed by the same package, had it stood for an equal length of time in a grocery store. Special mention is made of the moisture for the reason that in many powders, it constitutes one-third to one-fifth of what the purchaser gets for his money. The powders are divided into two groups:

Group I—

All powders containing abrasives or polishing material.

(a) Powder containing abrasives only.

(b) Powders containing abrasives and soap.

(c) Powders containing abrasives, soap and a softener.

Group II—

All powders not containing abrasive material.

(a) Powders containing nothing but "softeners."

(b) Powders containing "softeners" and soap.

By the term "softeners" is meant such substances as soda ash, borax and sodium phosphate, all of which are frequently used to decrease the hardness of water.

The methods used for determining the constituents are described below. The moisture content was determined by weighing five grams of the powder into a large tared aluminum dish, drying in an oven at 120° C. for five hours, and weighing the loss, calculating it as water.

In determining abrasive material such as sand, or volcanic ash, a sample of 0.5000 or 1.0 gm. was weighed into a beaker and washed several times by

decantation with boiling water to remove the soap, then with hot 1:6 HCl, after which the residue was washed onto a Gooch and dried at 120° C. If a qualitative examination shows that there is no soap present, the first washings with water may be omitted and the sample simply extracted with boiling HCl (1:6),

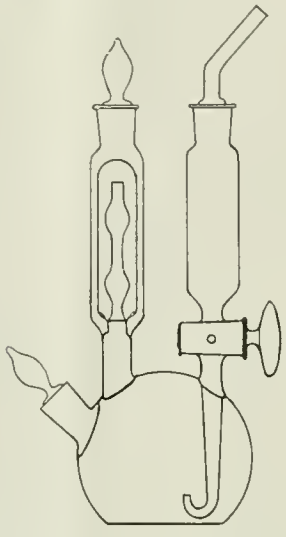


Fig. 1—Schroedeter Alkilimeter.

the residue dried, and weighed. If the powder contains soap, it must first be extracted by the treatment with water as otherwise the abrasive would be contaminated by the fatty acids, precipitated by the HCl.

The soap in each powder was determined by extracting a 2 gm. sample of the powder in a Wiley extractor with 95 per cent alcohol, as Na_2CO_3 and Na_2HPO_4 are both practically insoluble in 95 per cent alcohol, the sample of powder may be weighed directly into the Gooch, and placed in the extractor. After the soap has been completely extracted the solution is rinsed out, filtered into a platinum dish, evaporated to dryness on a water bath, dried at 100°, and the soap weighed. Unless redistilled alcohol is used it is best to use a definite volume, say 50 ccs., for each extraction so that a correction can be made for the dissolved matter in the alcohol. This correction is found by evaporating 50 ccs. of the alcohol, drying and weighing, just as in the determination of the soap.

No powders were found which contained both sodium phosphate and soap, so that to determine phosphate, it was only necessary to extract with water, acidifying if the powder contained sodium carbonate, and then precipitate the PO_4 in the usual way with magnesia mixture, filter, wash, ignite, and weigh as $Mg_2P_2O_7$.

The determination of Na_2CO_3 may be made in several ways. If the powder contains no other substances, a weighed sample is dissolved in water and titrated with N/10 acid, using methyl orange as an indicator. In the cases where the powder contained soap it was found practicable to extract the Na_2CO_3 with hot water from the residue after the soap extraction with alcohol. This water extraction was then titrated with acid as before. If the powder contains both Na_2CO_3 and Na_2HPO_4, it is necessary to correct the amount of acid used for the Na_2HPO_4 present as the Na_2HPO_4 reacts alkaline to the extent of one molecule of NaOH per combining weight.

$$Na_2HPO_4 + H_2O = NaOH + NaH_2PO_4$$

This correction is easily made after the determination of the Na_2HPO_4.

Before the actual work of analysis of the powders was begun, some experiments were carried out with a view to finding if possible, the quickest way of determining the CO_2 content of a mixture, and from this the Na_2CO_3.

Although the gravimetric method of liberating CO_2 by acid, absorbing in potash bulbs, and weighing the increase is known to be accurate, it is tedious in operation, requires rather elaborate and fragile apparatus, and is also subject to numerous errors.

The Schroedeter Alkilimeter, a sketch of which is shown, was tried out thoroughly and it was found that even with the most careful manipulation, the minimum error between two parallel determinations might easily be as high as 3 per cent. In testing out the apparatus it was carefully cleaned out, the drying tower filled with concentrated H_2SO_4, a weighed amount of Kahlbaum's C. P. Na_2CO_3, with enough H_2O to dissolve it, introduced into the bottom bulb and the tube for holding the acid which liberates the gas filled. The whole apparatus was then wiped dry,

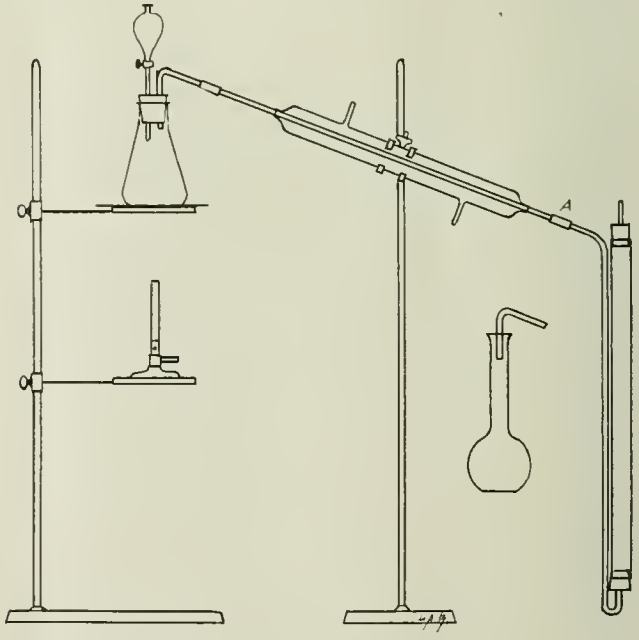


Fig. 2—Bower's CO_2 Apparatus.

placed in a dessicator, and allowed to come to room temperature. It was next weighed, care being taken to avoid touching with hands, so as neither to warm nor moisten it. The acid was then allowed to fall slowly upon the Na_2CO_3 solution so that the gas bubbled through the concentrated H_2SO_4 at the rate of about two bubbles per second. After ebullition

was complete, dry air was drawn through the apparatus to insure complete removal of the CO_2 and it was again weighed. The effect of using both HCl and H_2SO_4 for liberating the CO_2 was tried. Results are shown in the table below:

Wt. Na_2CO_3 taken	loss found.	loss calculated.	Error.
	CONCENTRATED HCl.		
1.000 gm.	0.6115 gm.	0.4153 gm.	+45%
1.000 gm.	0.2953 gm.	0.4153 gm.	—25%
1.000 gm.	0.5470 gm.	0.4153 gm.	+25%
	1:3 H_2SO_4		
.5000 gm.	0.2205 gm.	0.2076 gm.	6%
.5000 gm.	0.2232 gm.	0.2076 gm.	8%
.5000 gm.	0.2123 gm.	0.2076 gm.	3%

From these results it would seem that the apparatus works better when 1:3 H_2SO_4 is used for liberating the CO_2 than when HCl is used, but even with considerable care the results are at best only a crude approximation.

Several articles have recently appeared on the rapid volumetric determination of CO_2.* Of all of these, the apparatus proposed by Bowser, Fig. 2, appeared best adapted for the purpose, in that it was easily constructed, rapid in operation, and not liable to breakage. The method is briefly as follows: A solution of KOH 1:1 was made up and kept in stock for use. Exactly 10 cc. of this were pipetted into the absorbing tower for each determination, and a measured quantity of the material in which the CO_2 was to be determined, placed in the boiling flask. The whole apparatus was connected up, acid from the dropping funnel allowed to run slowly into the boiling flask, heating it at the same time. When ebullition was just beginning the acid was run in slowly, and the flask heated gently so that the rate of passage of the bubbles up the absorbing tower did not exceed 3 per second. The heat was increased gradually to boiling, and five or ten ccs. of liquid distilled over into the tower to insure the complete removal, and absorption of the CO_2. The tower was then detached from the condenser and the little bent tube inserted to facilitate blowing the liquid from the tower into a volumetric flask. The tower was rinsed out four times with water, which was sufficient to remove all of the alkali. The contents of the flask was made up to 100 ccs. and 25 ccs. aliquots taken for titration.

The principal upon which the titration is based is as follows: In the presence of an excess of NaOH all the CO_2 will be in the form of Na_2CO_3. Both NaOH and Na_2CO_3 are alkaline to phenolphthalein and methyl orange, but $NaHCO_3$ is acid to phenolphthalein and alkaline to methyl orange. Hence, if to the above solution acid is added until the pink color of the phenolphthalein disappears all of the NaOH will have been neutralized and all of the Na_2CO_3 changed to $NaHCO_3$.

TABLE I.

Name.	Moisture.	Volcanic Ash.	Soap.	Na_2CO_3	Na_2HPO_4	Na_2PO_4	Borax.	Sand.	Weight.	Price.	Est. Cost.
Nature's Polisher	0.97	.....	.....	.....	.....	.....	.....	87.82	1 lb.	10 cts.	$2.25
Bon Ami (albite)	0.28	93.18	6.54	.....	.....	.....	.....	.....	10 oz.	10 cts.	2.51
Lighthouse Cleanser	2.87	80.83	7.30	5.83	.....	.....	.....	.....	1 lb.	5 cts.	2.52
Swift's Pride Cleanser	3.54	80.52	14.75	.....	.....	.....	.....	.....	1 lb.	10 cts.	2.80
Gibson's Soap Polish	1.98	84.00	7.65	5.82	.....	.....	.....	.....	1 lb.	10 cts.	2.58
Volco Cleanser	1.85	93.51	3.69	.....	.....	.....	.....	.....	1 lb.	10 cts.	2.39
Polly Prim Cleanser	4.51	75.94	10.10	9.68	.....	.....	.....	.....	1 lb.	10 cts.	2.67
Wizard Cleanser	2.67	80.88	3.31	10.01	.....	.....	.....	.....	1 lb.	10 cts.	2.40
Old Dutch Cleanser	2.34	83.38	7.29	5.09	.....	.....	.....	.....	1 lb.	10 cts.	2.53
Sapolio	1.90	.....	13.40	3.15	.....	.....	.....	81.55	10 oz.	10 cts.	2.48
Larkin Water Softener	48.63	.....	.....	.....	.....	50.58	.....	.....	1 lb.	15 cts.	....
Wyandotte Cleanser	27.42	.....	.....	71.52	.....	.....	.....	.....	2 lb.	10 cts.	3.12
Sopode	26.23	.....	.....	55.32	18.17	.....	.....	.....	1 lb.	5 cts.	....
Rub No More	23.26	.....	.....	75.80	.....	.....	.....	.....	1 lb.	5 cts.	2.61
Hippo Powder	20.73	.....	.....	78.12	.....	.....	.....	.....	1 lb.	5 cts.	2.62
Borax Washing	28.85	.....	.....	66.67	.....	.....	4.66	.....	¾ lb.	5 cts.	2.51
Nine O'clock Washing Tea	21.33	.....	.....	77.57	.....	.....	.....	.....	1 lb.	5 cts.	2.62
Pearline	13.69	.....	30.86	55.41	.....	.....	.....	.....	½ lb.	5 cts.	2.83
Wizard Washing Powder	16.54	.....	13.24	68.38	.....	.....	.....	.....	1 lb.	5 cts.	3.08
Gold Dust	14.79	.....	35.02	49.00	.....	.....	.....	.....	¾ lb.	5 cts.	3.34
Star Naptha	13.36	.....	38.96	45.44	.....	.....	.....	.....	1 lb.	5 cts.	3.92

These figures have no other significance than that they represent the author's estimate of cost to the manufacturer and offer a relative basis of cost comparison.

$$2Na_2CO_3 + H_2SO_4 = 2NaHCO_3 + Na_2SO_4$$

If now a drop of methyl orange is added to the solution, it will still be alkaline to the methyl orange due to the $NaHCO_3$. If this solution is now titrated with standard acid until it is acid to methyl orange, the acid consumed will be equivalent to exactly one-half of the CO_2 originally present in the solution. As nearly all NaOH contains some Na_2CO_3, it is necessary to use exactly the same amount of NaOH each time and also to run a blank on it and subtract the CO_2 already present from that found in each determination. In practice 2N H_2SO_4 was used until the pink of phenolphthalein was almost discharged, then N/10 H_2SO_4 until the color disappeared, the burette read two drops of methyl orange added and the titration finished with the N/10 H_2SO_4. A complete determination may be made in this manner in thirty minutes and if several are run one may be titrated while the next one is distilling. 10

*A New Apparatus for Determination of CO_2, E. W. Gaither J. Ind. and Eng. Cham. Vol. 4, p. 649. A New Apparatus for the Volumetric Determination of CO_2, H. W. Brubaker, J. Ind. & Eng. Chem. Vol. 4, p. 559. Carbon Dioxide, Its Volumetric Determination, L. T. Bowser, J. Ind. & Eng. Chem. Vol. 4, No. 3. Volumetric Determination of CO_2 in Soils, L. T. Bowser, J. Ind. & Eng. Chem. Vol. 4, No. 4.

ccs. of 95 per cent ethyl alcohol added to the NaOH, Na_2CO_3 mixture before titration, increases considerably the sharpness of the end point with phenolphthalein. The chief objection to the method lies in the fact that methyl orange in the presence of such a large excess of Na_2SO_4 as is usually present, does not give a sharp end point, but a gradual fading from yellow to pink so that some little practice is necessary before the operator can hit the end point accurately. Practice does away with this difficulty to a large extent and the results are as satisfactory as those usually obtained by any other method. After some practice I was able to obtain results of about the following degree of accuracy on pure Na_2CO_3.

	CO_2 found.	calc.
.5000 gram sample	41.32%	41.53%
.2000 gram sample	42.15%	41.53%

In the soap powders in nearly all cases it was found possible to extract the Na_2CO_3 in water solution free from interfering impurities, so that it could be directly titrated. The above method as described can not be used when the mixture contains soap, as the fatty acids distill over to a certain extent, and since they do not have a very definite end point either with methyl orange, or phenolphthalein, they interfere and render the titrations inaccurate.

The analyses of the soap powders classified in the beginning follow in the order in which they come in the table.

To facilitate comparison, Table I has been compiled, showing at a glance the relative composition of the powders. The column in the table headed, "price" gives the price of the smallest package of that particular brand for sale, the weight of the package being given in the column immediately preceding. The column headed "estimated cost," was found as follows: the total price of the actual ingredients of each powder was calclulated based on the following figures, which, it is believed, are exceedingly liberal:

Na_2Co_2	0.8 cent per pound
Soap	4.0 cent per pound
Sand and Volcanic Ash	0.25 cent per pound
$Na_2B_4O_7$	3.5 cent per pound

No figures obtainable for Na_3PO_4 and $NaHPO_4$.

To the cost thus found was added 2 cts. (2c) to cover preparation, overhead charges and container, and these figures given under "estimated cost."

In connection with the Panama-Pacific International Exposition which will be held in San Francisco in 1915, there will be an International Engineering Congress, in which engineers throughout the world will be invited to participate. The congress is to be conducted under the auspices of the following five National engineering societies: American Society of Civil Engineers, American Institute of Mining Engineers, the American Society of Mechanical Engineers, American Institute of Electrical Engineers, and the Society of Naval Architects and Marine Engineers.

THE DETECTION OF CANE SUGAR IN HONEY.*

By CHARLES H. LaWALL.

By the above (query) I suppose is meant the detection of *added* cane sugar in honey, for it is an established fact that sucrose normally exists in cane honey to the extent of as high as 8 per cent, which is the maximum amount permitted by the standards of the U. S. Department of Agriculture.

There are no color reactions or simple chemical tests for the differentiation or distinction of any of the sugars and these are detected only by inferential tests based either upon the reducing power before and after inversion or by the optical activity under similar circumstances. As sucrose is chemically the same whether normally existing in the honey or in the shape of cane or beet sugar and as it is the amount rather than the actual presence which decides the genuineness of the article, the only tests of value are the quantitative tests, even were qualitative tests possible, which they are not.

The best method for the determination of cane sugar is by the use of the polariscope and the use of an algebraic formula in connection with the figures obtained for the optical rotation before and after inversion, observations being made at the same temperatures.

By inversion, of course, is meant the hydrolysis of sucrose which, when heated with diluted acids, is converted into dextrose and levulose, the levulose being in excess and the mixture of the two resulting sugars therefore possessing a levorotatory power in contradistinction to the dextrorotatory power of sucrose.

As honey consists largely of invert sugar (from 50 to 80 per cent), and as invert sugar is readily prepared from cane sugar in large quantities, it seldom happens that such a clumsy method of adulterating honey as by the addition of cane sugar direct is practised, when it is possible to convert the same sugar into invert sugar and thus simply add a sugar which is normally present in the honey. Invert sugar, like sucrose, is the same chemically, whether existing naturally or prepared artificially from sucrose, and it would be impossible to detect added invert sugar in honey were it not for the fact that in the process of inversion by any of the artificial methods, a small amount of furfuraldehyde is produced, and as furfuraldehyde is never present in genuine honey and as it can be detected in very minute amounts and with as great certainty as is the case with formaldehyde, it is customary to apply a test for the presence or absence of furfuraldehyde before deciding whether a honey is or is not genuine, even if the proportions and kinds of sugars are normal.

Such a test was years ago devised by C. A. Browne[1] and is as follows:

*Read at the June, 1913, meeting of the Pennsylvania Pharmaceutical Association.

Treat 5 cc. of a 1:1 solution of the honey in distilled water, in a test tube with 2 cc. of aniline acetate reagent (freshly prepared for the test by mixing 5 cc. of aniline and 5 cc. of water and adding just sufficient glacial acetic acid to make a clear solution), allowing the reagent to flow into the tube gently so as to form a separate layer upon the honey solution. If the tube be then gently agitated so as to slightly but not entirely mix the two layers a red ring or zone will be produced at the point of contact if furfuraldehyde be present, indicating the presence of added invert sugar.

Unfortunately this test is not infallible, for when pure genuine honey is heated (as, for instance, in the process of clarification when heat is sometimes used), furfuraldehyde is also formed and the test is of no value therefore unless applied to honey which has been known to never have been heated.

In conclusion I would say that it is not possible to detect cane sugar in honey in the sense of a qualitative test; that, as cane sugar is normally present in small amounts, its quantitative determination, preferably by means of the polariscope, becomes necessary; that the form in which sugar is added usually is that of invert sugar which can be readily detected in honey which has never been subjected to heat.

PLUMBAGO MINING IN CEYLON.

In a recent consular report, Consul Henry D. Baker gives the following description of plumbago mining in Ceylon:

Plumbago is Ceylon's most important mineral product, and in the exportation of plumbago the United States is Ceylon's most important customer, purchasing over one-half of the plumbago mined. The Ceylon customs returns show that in 1912 there was a total export of 654,650 hundredweight (hundredweight = 112 pounds) of plumbago from Ceylon, valued at $2,782,262, of which the United States took 310,255 hundredweight, valued at $1,318,587; Germany, the next best customer, 162,886 hundredweight, valued at $692,265; the United Kingdom, 107,595 hundredweight, valued at $457,274; and Belgium, 57,565 hundredweight, valued at $244,642.

Plumbago finds its use chiefly in the manufacture of crucibles for the steel trade. The value of the plumbago is largely determined by the percentage of carbon, while its structure and binding and refractory qualities are also important factors. Ceylon plumbago is known all over the world for its luster, lubricating, polishing, and binding qualities. In appearance it is a strong black crystalline, and in this respect it differs from the grayish lead which is found in young rock in America. The more refractory the lead the more suitable it is for crucibles.

There are now about 1,000 plumbago mines in Ceylon, including all the shallow pits, open works and deep mines. There are probably between 200 and 300 mines proper, the rest being shallow workings which last only a few months and are then abandoned. The depth varies from a few fathoms to as much as 120 fathoms. Most of the mines are worked by natives, the only important one controlled by Europeans being the Medapola. At the Medapola mine all the curing, grading, packing, and barreling is done at the mine but the produce of the native mines is shipped to Colombo, where it is mixed with lead to bring it up to a certain standard.

At the majority of the mines the only machinery used is the "dabare." This consists of a long wooden barrel with handles at each end. Round this a rope is given two or three turns and a bucket fastened to each end. It is worked by seven or eight men turning the handle. In a few places pumps are used for raising water, and two or three mines have engines for raising dirt, etc. Occasionally small fans are used for ventilating purposes.

The mines generally consist of a vertical shaft 8 or 9 fathoms deep or more sunk to cut the vein. The workings then go off on the underlay, the vein being opened out its entire length and taken down in one stage. Platforms are fixed at every 10 or 12 fathoms, on which "dabares" are placed for hauling. Means of ascent and descent are made by fixing poles across the vein and forming ladders. Excavating is done by blasting, generally with dynamite.

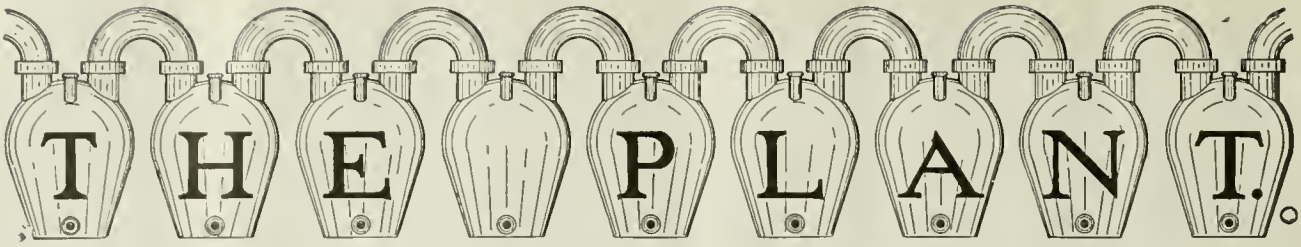
The vertical shaft is generally sunk through soft ground and requires timber. The timber consists of horizontal planks around the pit, held in place by vertical pieces, which are again held by "mukku" or poles across the ends and middle of pit, these latter being let into the vertical pieces. The whole is made tight by packing pieces and wedges behind the planks.

In the underlay or workings proper, which are generally in rock, no timber is required, but when necessary the supports consist of props fixed into the two walls at the proper angle. Where tunnels require timber, two props are set on the floor, a bar is placed on the top, and planks on these. Props and bars are set at intervals of a few feet, and planks run from one set to another.

In mining plumbago, it is merely raised from the ground and part of the rock separated. It is then carried in bags by coolies or bulls to a forwarding shed, where it is packed into barrels and forwarded to Colombo or elsewhere to be cured, that is, separated from stones, mica, or other associates by hand, and classified. The chief qualities are "lumps," "chips," "dust," and "flying dust." These are classified again according to quality.

Plumbago is a considerable source of revenue to the Ceylon Government, as there is an export royalty on it of 0.25 rupee per hundredweight (about 8½ cts. per 112 pounds). For the benefit of the industry the Government arranges for the inspection of every working plumbago mine once in six months.

[1] U. S. Dept. of Agriculture, Bureau of Chemistry, Bulletin 110, p. 68.



THE BY-PRODUCTS OF SUGAR MANUFACTURE AND METHODS FOR THEIR UTILIZATION.*

By C. A. BROWNE.†

Lectures delivered in previous years before the students of this course took up the "Chemistry of Raw Sugar Production" and the "Manufacture of Raw Sugar in the Philippine and Hawaiian Islands." Since these lectures have been printed in the School of Mines Quarterly, I will avoid repetition and save time by referring you to this journal for particulars regarding the chemical composition of sugar cane and the sugar beet and the methods of manufacturing raw sugar. As a subject for this lecture it appeared to me that a discussion of the by-products of sugar manufacture and methods for their utilization would fill up certain gaps that were not covered in the previous lectures, and so help to give us a broader survey of the sugar industry as a whole.

It may be stated as a general rule of all manufacturing that the number of by-products and the means for their utilization increase with the improvements in technical processes. This is particularly the case with the sugar industry. In the Philippine Islands we saw that the juice of the sugar cane was evaporated to a solid mass of concrete sugar which contained not only the sucrose, but the invert sugar, salts, amid, gums and other soluble ingredients of the cane.

Another example of raw sugar which contains the soluble impurities of the juice is the semi-liquid Jamaica sugar, which is sold in Kingston by the quart. When sugar is made by such primitive methods, there are no by-products and the question of their utilization is therefore a superfluous one.

The by-products of sugar manufacture in the more progressive countries are so numerous that it is possible to cover the field of their utilization only in the most superficial manner. In treating our subject we shall find it in many ways more convenient to subdivide it according to the character of by-product, as follows:

1. The utilization of the cellular refuse of beet and cane.
2. The utilization of the impuirities removed in clarification.
3. The utilization of the waste molasses.

UTILIZATION OF THE CELLULAR REFUSE OF BEET AND CANE.

In discussing this topic, we must bear in mind the differences between the physiological structure of these two plants, and also the differences in method of extracting the sugar.

The sugar beet is a pulpy root growing under ground. In harvesting the crop, the beet is dug up and the leafy top, together with the crown of the beet, cut off, after which the beets are transported to the factory. The leafy tops of sugar beets constitute a very important by-product which is usually utilized as a cattle food. In some cases, the beet leaves are simply dried, either in the open air if the weather permits, or else by mechanical driers; the dried leaves have the fragrance of the best hay and are much relished by farm animals. In many cases the beet leaves are converted into ensilage; the wilted leaves are tightly packed in silos and covered with earth to exclude the air; a lactic fermentation takes place w' converts the tops into a sour fodder something of the nature of sauerkraut. Access of air must be prevented; otherwise putrefactive changes take place with formation of butyric acid and other decompositio' products which give the ensilage a most unpleasant odor.

The pulp that remains in the diffusion batteries after washing out the sugar from the sliced bee' forms another very important by-product which is also used for feeding cattle. If there is a large cattle farm or ranch near the sugar factory, the wet pulp can be fed out just as it is emptied from the diffusion cells. The farmers who supply a sugar factory with beets frequently stipulate for a return of the beet pulp for feeding purposes, and a considerable amount of the pressed pulp is sent out from the sugar factories in freight cars, frequently to a distance of 50 or even 100 miles. In many cases the beet pulp is converted into ensilage and fed out to the stock according to requirement. The same precautions as to the silo must be followed as in making beet-leaf ensilage.

When local conditions are unfavorable for feeding the pulp or converting it into ensilage, many factories dry the pulp, using for this purpose the heat of the flue gas escaping from the boilers. The dried beet residue consists of a crisp brittle material which is packed in bags and sold as a cattle food; it is much relished by farm animals. Dried beet pulp swells up enormously when wet, so that care must be

*A special lecture in the Department of Chemistry, Columbia University, April 28, 1913, and reprinted in the School of Mines Quarterly.

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exercised not to permit animals to gorge themselves and then drink an excess of water. Death of live-stock has resulted from neglect of this precaution.

In the cane sugar industry a large amount of waste cellular matter also results from the harvesting and milling of the crop. The leafy portion of the cane top is sometimes fed to farm animals, and it has also been proposed to convert this material into ensilage, although I know of no such utilization upon an extensive scale. The green tip of the cane stalk, which is removed with the leaves in harvesting, is valueless for sugar making but is utilized for seed in most tropical countries, as stated in the last lecture. In Louisiana, owing to the limited period of harvest and the haste to get the cane all pressed before winter, no time is available for utilizing the cane tops; they are therefore left upon the ground and are afterwards burned.

The bagasse, or cellular matter of the cane stalk, which is left after milling, is very important by-product and many schemes have been proposed for its utilization. In most cane-producing countries the bagasse is used as a fuel to supply steam for the engines and heat for the evaporators. In many places the bagasse is the only supply of fuel available, and when this is the case other methods of utilization are impracticable. Bagasse, as it leaves the cane mill under good systems of extraction, contains about 50 per cent moisture and in this condition has a fuel value about one-quarter that of soft coal. The employment of bagasse as fuel has appeared to many a very wasteful procedure, and attempts have been made to use it in the manufacture of paper. It is obvious, however, that this method of utilization can be considered only when the value of bagasse as paper stock exceeds its value as fuel.

It has been demonstrated that paper of very excellent quality can be manufactured from bagasse, although the cellular structure of the cane may involve a considerable loss of cellulose, if the same methods of manufacture are followed as are employed with wood, straw, and other materials of coarse fiber. The cellular substance of sugar cane is very much like that of corn stalk and consists of about 75 per cent of fibrous cells and 25 per cent of pithy cells, the latter constituting the sugar-bearing tissue of the cane. The pith cells lack the felting property of the fibrous tissue; they are very easily disintegrated in the soda or sulphite digestion, which is ordinarily used in paper manufacture, and unless care is exercised are completely lost in the wash water. It was held at one time that the pithy tissue was valueless for paper making; this, however, is not the case. Cellulose made from the pith, while devoid of felting properties, has strong adhesive qualities upon drying out. Paper can be made, in fact, from the pith alone, and the product thus obtained has a strong resemblance to parchment in appearance and toughness. While the very best paper can be made from bagasse, but very little sugar-cane fiber is utilized at present for this purpose. The chief obstacles seem to be the great value of bagasse as fuel and the difficulty of securing skilled labor in the tropics.

Under good conditions of manufacture, four tons of wet bagasse will give one ton of paper, the value of which we may place at $20. Since four tons of bagasse equal one ton of coal for heating purposes, we may put the fuel value of this bagasse at $3, although this figure is much greater in countries where there is no coal supply. The value of bagasse, using the above figures, is therefore over six times greater for paper than for fuel. This ratio is reduced considerably, however, when we take into account the interest upon investment and the depreciation in value of the paper plant, as well as the direct cost of making the paper.

In this connection mention should be made of a new process which is being tried at present, which, if successful, promises to revolutionize present methods of sugar manufacture. This process consists in shredding the cane near the fields where it is cut, drying the shredded stalks, pressing the substance into compact bales, and shipping it to factories in the United States or elsewhere. The dry material is there extracted with water in diffusion batteries, and the sugar which is washed out is manufactured directly into refined sugar. The residue of fiber, in another department of the same factory, is made into paper. The promoters state that the paper is the product of most value from this process, the sugar being thus reduced in importance to a by-product. The sugar world is watching the developments of this new experiment with great interest.

UTILIZATION OF IMPURITIES REMOVED IN CLARIFICATION.

The quantity of filter-press cake obtained in sugar manufacture varies greatly according to the amount of lime and other agents used in clarification, and according to the purity of the juices. The amount of wet press-cake obtained in Java by the ordinary process of defecation was found to be about 1 per cent of the weight of cane; the press-cake contained about 70 per cent of moisture and 10 per cent of sucrose, whence the actual amount of impurities removed from the juice is only about 0.2 per cent of the weight of the cane. The material consists of fine particles of bagasse ground off in milling, with an admixture of wax, proteins, gums, lime sulphate and phosphate, iron oxide, and alumina, and considerable earthy matter which was brought in on the cane stalks from the field.

Where the carbonatation process of clarification is used, as is the case with beet-sugar manufacture, the press-cake is mostly calcium carbonate, the remainder consisting of the wax, proteins, gums, etc., found in defection press-cake.

Great benefit has been derived from the use of filter-press cake as a fertilizer, the nitrogen existing in a form which is readily available. The excess of cal-

cium carbonate in carbonatation cake has also been found beenficial upon certain soils. The employment of press-cake as fertilizer is about the only means of utilization, although attempts have been made in Java to use the cake from sugar factories as a source of wax. The percentage of cane wax in dried press-cake from the defecation process varies from 10 per cent to 20 per cent. To obtain this wax, the press-cake is dried in the sun or by heat of the flue gas, and extracted in percolators by means of naphtha; the latter is then distilled off for re-use and the residue of crude wax is purified by bleaching with chlorine. Sugar-cane wax is a hard brittle substance, resembling carnauba wax in appearance, and can be used as a substitute for the latter for many purposes. The present low price of wax has prevented this method of utilizing press-cake from making any advancement.

UTILIZATION OF WASTE MOLASSES.

The word molasses has many shades of meaning; chemically speaking, we may consider it as the sugar factory mother liquor from which a part of the sucrose has been crystallized. The molasses from the first crystallization may yield, upon evaporation, a second crop of sugar crystals, and the molasses from this may even yield a small amount of impure third sugar. The approximate average composition of beet and cane molasses, from which no more sucrose will crystallize, is given in the following table:

	Beet Molasses.	Cane Molasses.
Water	20.00	20.00
Sucrose	50.00	30.00
Invert sugar	Trace	30.00
Salts	10.00 (5% K_2O)	8.00 (4% K_2O)
Nitrogenous substances.	10.00 (2%N)	2.00 (0.4%N)
Gums, acids, etc.	10.00	10.00
	100.00	100.00

It is seen from the table that beet molasses is distinguished from cane molasses by a higher percentage of sucrose, by a much higher percentage of nitrogenous substances, and by a comparative absence of invert sugar. By treating beet molasses with the hydroxides of calcium, strontium, or barium, it is possible to precipitate the residual sucrose as an insoluble saccharate which, after filtering from the salts, nitrogenous matter and other impurities, is decomposed with carbon dioxide and the sucrose recovered in a pure form. In European countries a number of establishments make a special business of buying up beet molasses and recovering the sucrose by the strontium or other saccharate process. These technical processes of desaccharification belong, however, to sugar manufacture and we will not consider them as pertaining to by-products.

The table shows 5 per cent of potash and 2 per cent of nitrogen in beet molasses and 4 per cent of potash and 0.4 per cent of nitrogen in cane molasses; these figures suggest at once that molasses might have some value as a fertilizer; and such in fact has been demonstrated to be the case upon certain kinds of soil, more especially those deficient in humus. The application of molasses to other soils, however, has caused an acid fermentation with souring of the soil and loss of fertility, so that this method of utilizing molasses is not uniformly successful. But the greatest objection against this use of molasses is its wastefulness. There are more profitable methods of using the sugar and other organic solids of molasses than employing them as a supply of humus.

A second use for molasses is as a fuel. Molasses containing 20 per cent moisture has a thermal value about 3/8 that of coal. By means of specially constructed furnaces it is possible to secure a perfect combustion of the carbonaceous matter of molasses, 8 lb. of molasses supplying the same heat as 3 lb. of coal. A residue of ash, very rich in potash, is left and this can find a use either as fertilizer or as a raw material for making potash salts.

Molasses, as we have seen, contains 50 per cent or more of sugar, and the use of such a valuable food material as a fuel is wasteful if other more profitable means of its disposal are available. Unquestionably the most perfect utilization of molasses is as a food. The odor of beet molasses is enough to convince one that it is unfit for human consumption. Waste cane molasses is much more palatable, and many manufacturers of sirups make a business of bleaching it for table use. The exhausted molasses of cane sugar factories, with its accumulations of salts and other impurities, is not, however, a desirable article for sirup, and its use, whether bleached or blended, as a human food is not favored for this reason. Horses, mules, cows, and sheep, on the other hand, eat cane and beet molasses with great relish, and its use as a stock food, whether for working animals, for milk production, or for fattening, is attended with splendid results, provided over-feeding is avoided, which might cause derangement of the digestive system. The higher percentage of salts in beet molasses renders it somewhat less desirable as a cattle food than cane molasses.

The stable manure from animals fed upon molasses contains the valuable potash and nitrogen of the latter, and the use of such manure as a fertilizer has all the advantages and none of the disadvantages which result from the direct application of molasses to the soil.

Molasses is often fed in the liquid form, being either poured into troughs or sprinkled upon fodder. If it is desired, however, to market the molasses as a stock food, its use in the liquid forms is attended with several disagreeable features. Molasses is not a convenient material to transport or store, and the stock raiser also has difficulty in handling it when compounding his rations. Another objection is that animals become smeared and flies are attracted. To overcome the difficulties just named, it is the usual practice at present to mix the molasses with an absorbent filler, a sufficient quantity of the latter being used to keep the food dry and free from stickiness. The filler used for this purpose should have not only

a high absorptive power but also some nutritive value of its own. Finely cut hay and fodder are examples of such fillers; bran, meal, hulls, chaff, and similar products are also used. Peat and sawdust have been employed as molasses absorbents but such substances are objectionable on account of their low digestibility.

From the sugar manufacturer's viewpoint, the dried leaves and pulp of the sugar beet and the bagasse of the sugar cane make most excellent and convenient materials for preparing molasses feeds. By combining them with molasses in suitable proportions a successful utilization of two by-products is accomplished in one operation. A cattle food called molascuite, consisting of bagasse and sugar cane molasses, is shipped from the British West Indies to England in large quantities. Molasses alone in combination with a filler does not make a well balanced ration, so the usual practice is to incorporate with these a certain amount of corn, cotton-seed meal, brewers' grain, etc., to supply any deficiency in fat or protein. The percentage of molasses in mixed molasses feeds, according to analyses by Halligan, varies from 10 to 60 per cent. If more than 25 per cent of molasses is used the feed must be heated in driers to remove the excess of moisturre, which should not exceed 12 per cent. If too much moisture is present the feed becomes sticky and is very liable to spoil through fermentation.

One of the most common methods of using molasses is the manufacture of alcohol and rum. In many tropical countries the sugar house and distillery are side by side, and the chemist is required to have a practical knowledge of fermentation and distilling as well as of sugar manufacture.

In manufacturing alcohol from molasses, the latter is first diluted to a sugar content of about 12 per cent. This solution, or "wash," is usually acidified slightly with sulphuric acid to prevent the growth of injurious bacteria, and then, after adding yeast, is fermented until no further decrease in density is observed. The fermented liquid is then distilled and the alcohol or rum collected in receivers.

To secure the highest yield of alcohol, the temperature of the fermenting liquid should not exceed 30° C. (or 86° F.). In tropical countries, where the temperature of the atmosphere often exceeds this figure, the control of temperature during fermentation is often a difficult matter. A wash containing 12 per cent of sugar and started at 30° C. may, through the heat liberated during fermentation, reach a temperature over 40° C. Such temperatures in fact do occur in badly managed distilleries with great loss in efficiency from vaporization of alcohol and impairment of the vitality of the yeast. To prevent overheating of the fermenting liquid it is necessary to equip the vats with coils through which cold water can be circulated.

Two gallons of cane molasses should give a yield of one gallon 180-proof alcohol (90 per cent strength) which is the usual standard for denaturing. Such alcohol, according to the last quotations, has a commercial value of 38c per gallon. The cost of manufacture may be set at 8c a gallon, which leaves 30c as the value of the raw molasses, or 15c per gallon. Sugar-cane molasses in tank cars, according to the last New Orleans quotations, has a commercial value of 6c a gallon, so that there is a profit of about 9c a gallon in operating a molasses distillery, provided the output of denatured alcohol finds a ready market, which at present is not always the case. The present high price of denatured alcohol prevents its competing with gasoline, and other petroleum products, as a source of power, light, or fuel.

In tropical countries the distiller of molasses must turn his attention almost entirely to the manufacture of rum. A good quality of rum, containing 80 per cent alcohol, will usually net the distiller over 50c a gallon. In the Island of Jamaica, which is noted for its rum, I was informed that it takes about 15 lb. of sugar in molasses to make one gallon of rum. This is equivalent to a return of over 3c a pound on the uncrystallized sugar of the molasses, a value often higher than the return upon the crystallized sugar.

Although we may not advocate its use as a beverage, rum is a commercial product which the food chemist is called upon to inspect, analyze, and in other ways to reckon with. A few words may therefore be devoted to the methods peculiar to rum manufacture. Rum is valued not simply by its alcoholic content but also by its flavor. The production of flavor is in fact one of the chief objects of the rum distiller, and a peculiar mystery often shrouds this phase of the process. As an example of the manner in which high-flavored rums are produced, the following process, as used in Jamaica, will be described.

The flavor of rum is due to the presence of alcoholic esters of acetic, butyric, and other higher fatty acids; the first requirement in the production of flavor is the formation of the acids for esterification.

Acetic acid is prepared by allowing cane juice, skimmings from the clarifiers of the sugar house, and other refuse, to undergo an alcoholic fermentation, and then pumping the liquid on to cane trash in cisterns. An acetic fermentation sets in, just as when cider is poured over shavings in the quick vinegar process, and the solution becomes strongly acid.

For the production of butyric, caprylic and the other fatty acids, a putrefactive fermentation is necessary, and this is carried out by dumping the dead yeast from the stills, cane refuse, lees from the retorts, and other adventitious matter, into a receptacle called the "muck hole." A putrefactive fermenation sets in with formation of butyric and other fatty acids. To neutralize the excess of free acid, which would retard fermentation, powdered marl is added from time to time. When the liquid in the muck hole is ripe, it is added to the acid cisterns, the free acetic acid thus liberating the butyric and other acids from

their lime salts. The mixture of acids, thus produced, constitutes the basis for flavor production.

In conducting the fermentation, the wash is prepared by mixing molasses, skimmings, and cane juice with a certain amount of "dunder," which is the spent liquor obtained from the stills after distillation. The dunder is rich in nitrogenous compounds and salts, and serves as a nutrient for the growth of the yeast. After fermentation has begun, a requisite amount of the acid flavoring mixture is added; a part of the alcohol, formed by the action of the yeast upon the sugars, unites with the acids of the flavor to produce ethyl acetate, ethyl propionate, ethyl butyrate, and the other higher esters, all of which, passing over with the alcohol when the wash is distilled, give the resulting rum its characteristic aroma and flavor. High flavored Jamaica rum may contain as high as 1 or 2 per cent of esters, while the low flavored rums contain less than half of this amount. Over 95 per cent of the esters consists of ethyl acetate; the remainder is principally ethyl butyrate, the ester of chief importance as regards flavor production, with small amounts of other fatty acid homologues.

Leaving now the manufacture of rum, we will close our subject by considering briefly some of the methods for utilizing sugar-beet molasses. Germany has made the greatest advancement in this regard. Of a total production of 400,000 tons of beet molasses in Germany, about 55 per cent is desaccharified for sugar production, about 30 per cent is used as a cattle food, about 10 per cent is fermented into alcohol and the remaining 5 per cent is utilized in various miscellaneous ways. Among the latter we may mention the use of molasses for manufacturing dye stuffs, shoe blacking, yeast, moulds and briquettes, and numerous other commodities.

The residues from the desaccharification factories, best known under its German name of molasses *schlempe* has been a subject of special study from the standpoint of utilization. If we subtract the sucrose from the composition of beet molasses given in the previous table, we shall form a fair idea of the composition of *schlempe*. From 1,000 kg. of beet molasses are obtained about 350 kg. of concentrated *schlempe,* containing about 30 per cent of mineral matter, mostly potash salts, some 20 per cent or more of nitrogenous substances, and a remainder of acids, gums, caramelization products, and other organic residues.

Molasses *schlempe* contains 12 to 15 per cent of potassium and 4 per cent or more of nitrogen, and its conversion into derivatives of these elements constitutes at present the chief method of utilization. The *schlempe* is first heated in retorts, by which means it is decomposed into a mixture of volatile products consisting of carbon dioxide, carbon monoxide, hydrogen, nitrogen, methane, ammonia, methyl amine, methyl alcohol, water, and other substances. The volatile decomposition products escape from the retorts at a temperature of about 400° C. and are led through a system of tubes heated to a temperature of about 1,000° C. The effect of this heating is to convert the volatile nitrogenous compounds into ammonium cyanide, the gas after cyanization containing about 7 per cent NH_3 and 7 per cent HCN. After leaving the hot tubes, the gases, which are always kept under reduced pressure, are cooled, freed from tar, and then washed over sulphuric acid to break up the ammonium cyanide, the ammonium sulphate, which is formed, being recovered. The hydrocyanic acid is then absorbed in water and the residue of combustible gases is led back to the furnaces for heating the retorts. The hydrocyanic acid is then distilled, and absorbed in sodium hydroxide; the solution of the latter, after evaporating and crystallizing, yields solid sodium cyanide.

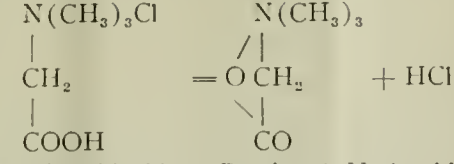
By the above method about three-fourths of the nitrogen in molasses *schlempe* is recovered as ammonium sulphate and sodium cyanide, the remaining one-fourth escaping as gaseous nitrogen. A small amount of pyridine is also obtained by this process, in connection with the ammonia. The residue of mineral matter in the retorts, after distilling the *schlempe,* is worked up into potash, of which some 15,000 tons are made annually in Germany from this source.

Two factories in Germany produce annually, by the process of distillation described, about 5,000 tons of ammonium sulphate and 5,000 tons of sodium cyanide, with a commercial value of about $1,750,000. The sodium cyanide thus manufactured is nearly all exported to the Transvaal, where it is used for extracting gold by the well known cyanide process.

Chemists in Germany are making further efforts towards improving the utilization of molasses *schlempe*. By the present methods of distillation, about one-fourth of the nitrogen is lost, and this is wasteful from the standpoint of highest economy. It has been felt by some chemists that efforts should be made towards removing some of the valuable organic constituents of the *schlempe* before making the distillation. Among the more important of the nitrogenous organic substances, we may mention 10 to 12 per cent of betaine, 5 to 7 per cent of glutaminic acid, 1 to 2 per cent of leucine and isoleucine, and various other amino acids, neucleine bases, etc. The separation of these compounds from the *schlempe* does not seem to be a difficult one. Search is being made for uses to which these substances may be put, and with the discovery of such uses we may look for greater refinements in the processes of utilization.

As an example of the specific uses to which the nitrogenous components of beet molasses may be put, we may mention that betaine is now prepared in Germany from molasses *schlempe* by extracting with alcohol and is marketed as crystalline betaine chloride under the pharmaceutical name of "acidol." Betaine chloride, when dissolved in water, is decomposed into

betaine and free hydrochloric acid, according to the formula:



Betaine chloride = Betaine + Hydrochloric acid

This property of betaine chloride offers a convenient means of giving hydrochloric acid medicinally in the form of a powder or pills; tablets of betaine chloride and pepsin under the name of "acidol-pepsin," are now prescribed for indigestion.

In the early days of sugar manufacture, the molasses and other by-products were regarded for the most part as useless encumbrances, and were disposed of by dumping into the ditch or the nearest stream; and these conditions still exist in very primitive countries. It is surely a great step from such a wasteful procedure to the methods of utilization practiced at present in the leading sugar producing countries.

IMPORTANT ALLOY OF STEEL.

The chromic iron ore produced and sold in the United States was nearly 70 per cent greater in 1912 than in 1911, according to J. S. Diller, of the United States Geological Survey, in an advance chapter—"The Production of Chromic Iron Ore in 1912"—from "Mineral Resources." The total output marketed in 1912 was 201 long tons, valued at $2,753, compared with 120 tons, valued at $1,629, in 1911. California is the only producing state, and the output comes from three separate deposits. Two new mines were opened, one near Livermore, in Alameda County, and the other near Piedra, in Fresno County.

More chromium ore is now used in the United States in chemistry than for metallurgy; it is consumed in the manufacture of pigments, dyes and various chemical compounds, and also in tanning light leather, rendering it tough and resistant to moisture. Most chromium pigments are very permanent. Chromium is used metallurgically in making chromium alloys and furnace linings, the latter either in the form of chrome bricks or of irregular coarse and fine fragments of chromite hammered into place without the use of cementing material.

The use of chromium in making alloys is extensive. Chromium gives to steel a marked degree of hardness, and if added in the proper proportion it does not produce brittleness. Chromium steel alone or alloyed with tungsten or molybdenum is used for making high-speed tools. It is also used in the manufacture of files, ball bearings, armor plates, and armor-piercing projectiles, for which it is generally alloyed with nickel, vanadium, or manganese.

The United States has never been a large producer of chromic iron ore. Its maximum annual production in 1894 was nearly 4,000 tons.

A SYNTHETIC TANNIN.*

By EDMUND STAISNY, PH. D.

It has always been the desire of chemists to replace natural products by artificial substances, and especially those which are used for technical purposes. The object of doing so is to make the industry more independent of the market for natural products in general, further to obtain economical advantages, and finally to achieve results which may modify or surpass those obtained by the use of natural products. This desire to find artificial substances for technically important materials has led to the invention of artificial dye-stuffs, perfumes, silks, synthetic indigo, rubber, etc., and tends to reduce the number of indispensable natural products to a very few, such as coal, salt, ores, water, air, etc.

There is one group of natural products which has not yet been successfully substituted by synthetic substances, viz., the vegetable tannins. Though chrome tannage has been, and will be, an important competitor of vegetable tannages, still the largest amount of leather is made by means of vegetable tannin materials and tannin extracts, and it seems rather unlikely that one could find an artificial substitute for these substances which will be able to compete with these both in effect and in price.

In speaking of artificial or synthetic tannins, one must distinguish between substances which are identical as to chemical constitution with the original tannins (as synthetic indigo is identical with purified natural indigo), and with tannin substances which show only analogies and resemblances in their constitution and chemical behavior without being identical with the natural products, but which are capable of converting hide into leather (such substances could be comparable with aniline dyes as substitutes for natural dye-stuffs).

The first alternative, *i. e.*, the attempt to synthesize substances exactly identical with tannins as to chemical constitution involves considerable difficulties. In the first place, our present knowledge of the chemistry of vegetable tannins is rather insufficient since the constitution of most tannins, and especially of those of great industrial importance, is still an unsolved problem. The constitution of gallotannic acid, the tannin of galls, has been solved now by E. Fischer and his pupils. Catechin, the slightly soluble substance present in gambier, has been successfully investigated by Kostanecki and others, and if ellagic acid can be called a tannin, it concludes the series of those which are chemically understood. E. Fischer has embarked upon a very promising attempt to synthesize gallotannic acid, but these experiments—though extremely interesting and valuable from the scientific point of view—can scarcely lead to results of technical importance, as the price of such products

*From The Leather World, March 20, 1913, and Cellegium, April, 1913.

would be very much higher than the price of the natural material.

We have, therefore, to go back to the other alternative, *i. e.*, to attempt to synthesize substances of a constitution similar to, though not identical with, the vegetable tannins, and with the property of converting hide into leather. This problem again is connected with the question of the nature of the tanning process, and we all know that this latter question is not yet solved. Some of us assume the tanning process to be a chemical combination between hide and the tanning agent, either the formation of a salt or a condensation product of a more complicated form, others again—with whom I am inclined to associate myself—emphasize the semi-colloidal character of every tanning agent, assuming that the tannin is primarily absorbed, and then undergoes secondary changes on the hide fiber, without actually combining with it. From this view the artificial tannin must be similar in physical properties, and especially in its semi-colloidal character, as well as in chemical constitution, to the natural product.

It has been the object of many years' work to find a way of producing sucs substances, which could be cheap enough to be of more than theoretical interest. The solution of this problem—or at least one solution of it—has been achieved by the action of formaldehyde on phenolic bodies under such conditions that only water soluble products are obtained. The action of formaldehyde on phenols, it is true, has been made the object of several investigations, and is the subject of various patents, but in most of these processes the products of the synthesis are entierly or partially insoluble in water and are used as substitutes for resins, celluloids, etc.

Other patents again describe the action of formaldehyde on phenols in neutral or alkaline solutions, whereby phenol-alcohols are produced which have no tanning properties. If, however, conditions are chosen so that only water soluble substances are formed in an acid solution, the products of synthesis are very similar to vegetable tannins, not only in their physical properties, but also in respect of some of the most characteristic chemical tests, and last, but not least, as regards the tanning capacity. Obviously subtsances of such origin will contain a carbon bridge combining two phenolic nuclei, and it may be pointed out that the same general structure is not at all unlikely to be due to some of the natural catechol tans, which thereby may differ from the pyrogallol tans.

As an example how such artificial tannins can be produced, the following method of working may be quoted (see the author's Austrian patent No. 58405): —Take a phenol, *e. g.*, crude cresylic acid; heat it with the equivalent amount of sulphuric acid for a few hours to 100-120° C.; cool down, and add slowly while cooling and stirring, 1 molecule of formaldehyde to each 2 molecules of the phenol. The product obtained in this simple way is of a pasty nature, and after neutralizing the free mineral acid with alkali forms the synthetic tannin called "Neradol," showing the following properties:—It is easily and completely soluble in water, the solution being very little colored. The semi-colloidal character of the solution can be seen in dialytic experiments, and by the non-crystallizing nature of the substance. Gelatine solutions produce a precipitate, ferric salts give deep blue color, lead salts and aniline hydrochloric also give precipitates.

The most important analogy with vegetable tannins, however, lies in the fact that "Neradol" is capable of converting hide into leather. This has been proved by a great number of experiments both on a small and commercial scale, and it seems that there are many possibilities for the application of this tanning agent, both alone and in combination with other materials. The white color of the "Neradol" tanned leather, and the brightening and bleaching effect of "Neradol" when used in combination with other tannins (vegetable or chrome) may be specially mentioned.

The problem of finding artificial organic tannins, similar to, if not identical with, natural vegetable tannins, has thus found one solution, and it is to be hoped that the introduction of the above-named product, followed by other synthetic tannins, may in the future lead to a development in the leather industries similar to that brought about in the dyeing industries by the introduction of artificial coloring matters.

NEW METALIZING PROCESS.

Some interesting experiments have been carried out in Glasgow with the Ostermann system of "metallizing" all kinds of materials. The plant was installed in the works of Stewards & Lloyds, and during the experiments a considerable number and variety of articles in metal, glass, paper, wood, and stone were coated with metal, so that when the articles were bent or hammered the coating showed no signs of bursting or peeling. Zinc, lead, tin, aluminum, copper, bronze, nickel, or alloys of any of them are forced in an atomized condition from the nozzle of the machine employed upon the surface under treatment.

It is claimed for the system that it can be applied to many purposes for which galvanizing is unsuitable, especially to the coating of ships' bottoms and other large steel structures; that it can be used also for coating very light materials, such as the woven fabrics of aeroplanes or airships, and that it affords a guaranty against corrosion. Although new in this country, the system, it is said, has found considerable favor in Germany, where a large number of installations have been ordered by the government for use in warship work.—London Times Engineering Supplement.

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48th Annual Meeting of American Chemical Society.

The 48th annual meeting of the American Chemical Society will be held in Rochester, N. Y., Sept. 9th to 13th, inclusive. A meeting of the council will be held on Sept. 8th, at the Hotel Seneca, immediately following the complimentary dinner to be given to the council at 7 o'clock.

The program will open with a general meeting on Tuesday at 10 a. m., in the assembly hall at Kodak Park. Members should make a special effort to be present at this opening meeting, as it will not only be one of the most interesting meetings of the session, owing to the fact that it will contain the general addresses, but the whole day will be one of special features, inasmuch as the members of the society are to be the guests of the Eastman Kodak Company at luncheon following the morning meeting, and the afternoon will be spent in visiting the immense plant of the Eastman Kodak Company at Kodak Park. This will be the only opportunity to visit the Eastman Kodak Company. As the company is making special efforts to entertain the membership, it is hoped that every member will endeavor to be present at this first session.

There are already signs that the meeting this September will be the largest that the society has ever held as a separate organization, and it is probable that from 700 to 1,000 chemists will be present. All divisions will meet; and the biological section will be duly organized as a division, electing its officers on Friday morning.

A smoker will be held at 8:30 p. m., Tuesday, in Masonic Hall. The divisional meetings on Wednesday, all day, and Thursday and Friday mornings, will be held in the Eastman building, University of Rochester. The President's address will be given at the East High School, Rochester, at 8 p. m., Wednesday; and the subscription banquet, Thursday night, at 7 p. m., at Powers' Hotel.

On Thursday and Friday afternoons excursions will be open to the following manufacturing plants: Bausch & Lomb Optical Co., Taylor Instrument Co., Curtice Bros Co., J. Hungerford Smith Co., Moerlback Brewery, German-American Button Co., Genesee Reduction Co., Municipal Incinerator, Stecker Lithographic Co., and possibly others.

The local committee is made up as follows:

General: V. J. Chambers, F. R. Baxter, H. E. Howe, Harry LeB. Gray, J. O. Schlotterbeck, Ernest Little, J. E. Woodland, and the following chairmen of sub-committees: Finance, F. W. Lovejoy; Registration and Information, H. A. Carpenter; Arrangements, Ernest Little; Press, A. E. Crockett; Banquet, C. F. Hutchinson; Entertainment, M. H. Eisenhardt; Ladies, Miss Lattimore; Factory Excursions, J. E. Woodland; Vacation and Side-Trip, H. LeB. Gray.

PAPERS FOR MEETING.

All papers for the meeting must be in the Secretary's hands on or before Aug. 22, or in the hands of secretaries of divisions by Aug. 20, in order to be on the program. Especially the secretary of the organic division requests that organic papers be sent direct to him. By vote of the council, no papers can be presented at the meeting that are not printed on the final program. The following are the addresses of the divisional and sectional secretaries:

Agricultural and Food—G. F. Mason, care of Heinz Company, Pittsburgh, Pa.

Biological—I. K. Phelps, Bureau of Mines, 40th and Butler Sts., Pittsburgh, Pa.

Fertilizer—J. E. Breckenridge, Carteret, N. J.

Industrial—S. H. Salisbury, Jr., Lehigh University, South Bethlehem, Pa.

Organic—Wm. J. Hale, University of Michigan, Ann Arbor, Mich.

Pharmaceutical—Frank R. Eldred, 3325 Kenwood Ave., Indianapolis, Ind.

Physical and Inorganic—R. C. Wells, U. S. Geological Survey, Washington, D. C.

Rubber—Dorris Whipple, care of the Safety Insulated Wire & Cable Company, Bayonne, N. J.

Water, Sewerage and Sanitation—Edward Bartow, University of Illinois, Urbana, Ill.

Apparatus and materials will be supplied to those wishing them for demonstration purposes. It is particularly important that the secretary be informed of any papers requiring a lantern for their illustration.

VACATION AND SIDE-TRIP COMMITTEE.

Attention is called to a new committee in connection with our next meeting in Rochester, namely a Vacation and Side-Trip committee, whose object is to furnish information to those desiring it relative to train and boat connections in and out of Rochester and automobile trips. The committee desires to call attention to the Canadian National Exhibition at Toronto, August 23 to September 9. It is of the utmost importance that those intending to visit the exhibition in connection with the Rochester meeting secure accommodations in Toronto at the earliest possible time. Full information can be supplied by this committee. Address H. LeB. Gray, Eastman Kodak Co., Rochester, N. Y.

FINAL PROGRAM.

The final program will be sent to all members of the Rochester Section, to secretaries of local sections, to members of the council, and to all members who make special request therefor by postal card to this office. The expense of printing and mailing this program is so great that it will be sent only to those who especially desire it on account of their intention of attending the meeting. Other members will find it printed in the society's journals.

ABSTRACTS OF PAPERS.

Abstracts of papers should be prepared and brought to the meeting, or, even better, sent to the secretary in advance thereof. Members sometimes fail to realize how important this is to the success of the society and to the proper advertisement of the meeting itself. Unless abstracts of the papers are brought to the meeting and early placed in the secretary's hands, there is no opportunity for proper publicity in the local press, which is of very great advantage to the society. Members will greatly aid the secretary's office by remembering this fact.

HOTELS.

The Hotel Seneca has been selected by the local committee as headquarters. It is essential that accommodations for the meeting should be secured at the earliest possible moment, as another convention is to be held in Rochester during the week of September 8, and members of the society coming without previously having secured rooms may be seriously inconvenienced.

ENTERTAINMENT OF VISITING LADIES.

During recent meetings, and especially at the annual meeting, the number of visiting ladies has tended to increase; and it is hoped that many of the members will bring ladies with them to the Rochester meeting. Every effort will be made to make their stay in Rochester an enjoyable one, and the local committee has outlined the following additional entertainment for the ladies who are present:

Tuesday, September 9, 8:30 p. m., card party, Century Club.

Wednesday, September 10, 10 a. m., complimentary excursion to Irondequoit Bay and luncheon at the Newport House, full day trip.

Thursday, September 11, 9 a. m., auto excursion of 45 miles about parks and Irondequoit gardens.

INDUSTRIAL DIVISION ANNOUNCEMENT.

The secretary of the Industrial Division, Mr. S. H. Salisbury, Jr., Lehigh University, South Bethlehem, Pa., wishes to announce that a new descriptive directory of the division will probably be issued the latter part of this year, provided members do their part toward its preparation and publication. In order that the directory may be a success, it is necessary for all members engaged in industrial work who are, or wish to be, registered in the industrail division, to send to Mr. Salisbury their present address and the occupation in which they are engaged, together with the lines of industrial chemistry in which they are most interested. It is also very essential that this information be accompanied by a contribution of $1.00 toward the expenses of the division and the publication of the directory.

It is hoped that members will endeavor to arrange their summer vacations so that they can be present at the Rochester meeting, which is certain to be one of the most enjoyable ever held by this society. Charles L. Parsons, Box 505, Washington, D. C., is secretary.

24th General Meeting of the American Electrochemical Society.

The 24th general meeting of the American Electrochemical Society will be held in Denver on Sept. 9, 10 and 11, 1913.

The special train with the Eastern members is expected to arrive at Denver on Sept. 8. Automobiles will take the party for a ride about the city's compresive park and boulevard system, finishing at the Hotel Shirley, the society's headquarters. In the evening of Monday there will be registration, a meeting of the Board of Directors and a general good time of getting together. The program includes the following:

Tuesday, Sept. 9—A morning session will be held in Denver for the reading and discussion of papers. For the afternoon various visits are being arranged. In the evening an informal smoker will be held.

Wednesday, Sept. 10—An early car will be taken for Boulder, where a session for the reading and discussion of papers will be held at the University of Colorado. After lunch automobiles will be taken up Boulder canyon to the power plant of the Central Colorado Power Company, at the entrance to the Boulder tungsten district.

Thursday, Sept. 11.—In the morning a session will be held for the reading and discussion of papers at the School of Mines in Golden. For the afternoon

various visits are being arranged. In the evening an informal picnic dinner will be held on Lookout Mountain, just west of Denver, behind Golden.

The program of papers to be presented and discussed in the three sessions at Denver, Boulder and Golden will be announced in the next *Bulletin* of the society. The potentialities of the applications of electrochemistry in Western metallurgy will naturally be prominent in the program.

Various visits are being arranged to places of great chemical and metallurgical works; there will be much of interest and also some matters of decidedly novelty.

For the ladies' entertainment during the three days in Denver a trolley ride to the Foot Hills of the Rocky Mountains, a luncheon and a theater party have been outlined with other rides and visits to places of interest.

Friday, Sept. 12—In the morning the return trip will be begun which will take the party first to Colorado Springs, where the forenoon will be spent in a visit to the Garden of the Gods or places of metallurgical interest. In the afternoon a trip will be made up Pike's Peak, where it is intended to hold the concluding session of the meeting, the program of which will be announced in the next *Bulletin* of the society.

Saturday, Sept. 13—A further side trip will be made from Colorado Springs over the magnificent "Short Line" into the gold district of Cripple Creek.

On Saturday night the special train will start from Colorado Springs on the return trip to the East.

According to present indications the attendance will be large and it is hoped that it may be possible to start a special train right from New York City. The trip from New York to Denver will be made over the New York Central and Burlington lines, the return trip on the Sante Fé. The train will be composed of the highest grade Pullman equipment, drawing-room, compartment, observation and dining-cars; also a combination buffet smoking-library car with barber shop and bath. The entire train will be electrically lighted and all steel equipment will be used.

The complete schedule of the special train (which will be the first electrochemical train ever arranged) will be published in detail with connections from other cities, details of fares, in a pamphlet to be issued shortly.

The special train will leave New York City from Grand Central Terminal on Saturday, Sept. 6, at 10:30 a. m., arrive Chicago on Sunday 7:59 a. m., leave Chicago at 9:45 a. m. and arrive in Denver on Monday, Sept. 8, at 1:15 p. m.

The return train will leave Colorado Springs on Saturday, Sept. 13, at 10:30 p. m. (Western time), arrive Kansas City on Sunday at 6:55 p. m., leave at 7:30 p. m., arrive Chicago on Monday at 9:15 a. m., (Central time), leave Chicago at 10:15 a. m., and arrive in New York City on Tuesday, Sept. 16, at 9:11 a. m.

All requests for Pullman car reservations and railroad transportation should be made to the chairman of the Transportation Committee, Mr. J. M. Muir, 239 W. 39th Street, New York City, from whom any additional information concerning transportation may be obtained.

Dr. J. W. Richards, Lehigh University, South Bethlehem, Pa., is the secretary of the American Electrochemical Society.

American Mine Safety Association.

The annual meeting of the American Mine Safety Association, composed of leading coal and metal mine operators, mining engineers, mine-safety engineers and mine surgeons, will be held in Pittsburgh, Pa., September 22-24.

This association, which held its first meeting a year ago, has for its purpose a reduction of the number of accidents in the mines and quarries (3,602 in the year 1911) and the alleviation of the more than 60,000 men who are injured each year.

American Mining Congress.

Manufacturers of mining machinery, rescue and first-aid apparatus and safety appliances are to be given an opportunity to display their wares before the mining men of the country at a great industrial exposition to be held under the auspices of the American Mining Congress in Philadelphia, Pa., the week of October 20.

This exposition, the first of its kind in this country, will be held in conjunction with the annual convention of the Mining Congress and the double attraction is expected to attract thousands of interested men. It will be entirely national in scope, the metal mining interests of the west to be as fully represented as the coal mining of the east. In fact, there is a tentative plan to have a gold mining camp in full operation with a mill crushing the ore. Horticultural Hall, the biggest place of its kind in Philadelphia, situated in the heart of the city, has been engaged for the occasion.

While the plans are still in embryo, a number of the leading manufacturers have already been approached and have shown sufficient enthusiasm to lead to the belief that all of the space will be taken in a short time and that there may not be enough to take care of all who apply.

A number of the big coal companies that have developed the "Safety First" movement at their mines are now negotiating for large amounts of space to show the mining men and the public what they are doing in behalf of their men. These companies will send rescue and first-aid crews, and there is talk of exhibition drills between the various crews. The United States Bureau of Mines will be represented by one of its safety cars and a picked crew of helmet men. The state of Illinois and a number of the big anthracite companies may send rescue cars for exhibition purposes.

Asphalt Obtained from Oil.

Until recently the popular idea of asphalt represented the solid material found in certain veins in Utah, or obtained from the shores of the Dead Sea, or from the asphalt lake in the Island of Trinidad, the material being used for asphalt varnish or for street pavement.

Within the last few years, however, the asphalt trade has been dominated to a steadily increasing extent by a different variety of asphalt obtained by boiling down the heavy petroleum found in California and in the region of the Gulf of Mexico to a semisolid material which has found wide use for roofing purposes and as a binder in modern road construction. A total of 333,213 short tons of this oil asphalt was made in 1912 and had a value at the points of production of $3,534,077. This is a gain of 33.7 per cent over 1911, and is nearly three times as much as the output of all other kinds of asphalt taken together, as shown in the annual report by David T. Day, of the United States Geological Survey, published as an advance chapter from Mineral Resources for 1912.

Asphaltic oils differ very widely in the proportion of asphalt contained, ranging from oils having no asphalt to very viscous oils which are suitable for road material with practically no refining. Such natural liquid asphalt is known in many localities, especially near Lander, Wyo. It has not yet come into popular use, as asphaltic residues of exactly the required consistency may be obtained more cheaply by boiling down the thinner asphaltic oils characteristic of many regions in Texas, California, and Mexico.

The proportion of asphalt contained in the asphaltic oils of California, Texas, and Oklahoma varies within wide limits. The oils of the Coalinga district, California, vary from 1.89 to 57.42 per cent.

In the Kern River field there is a variation between 16.2 and 38.7 per cent. In the Sunset-Midway-McKittrick region the variation ranges from 11 to 51 per cent, in the Los Angeles field from 13.3 to 42.2 per cent, and in the Santa Maria field from 12 to 42 per cent. In Texas and Louisiana the asphaltic oils, which are limited practically to the region of the Gulf coast, show variations from no asphalt to a maximum of 20 per cent.

WANTED—Position as chemist, technical education, 8 years' practical experience, fair salary to start. Address W. HENRICHS, 520 Beyers Ave., Joplin, Mo.

SITUATION WANTED.—Wanted by junior chemist, position as laboratory assistant or analyst—advanced I. C. S. student with 2 years practical laboratory and foundry experience. Box 102, care Chemical Engineer, 608 So. Dearborn St., Chicago, Ill.

WANTED.—A chemist who has had some experience in the making of a general line of pastes and gums. A good opportunity for the right man. The Independent Glue & Gelatine Co., 2176 E. 18th St., Cleveland, O.

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THE CONDENSATION OF GASOLINE FROM NATURAL GAS.*

By GEORGE A. BURRELL† and FRANK M. SIEBERT.‡

In this paper are given some results of work performed by the Bureau of Mines having to do with the condensation of gasoline from natural gas.

CHEMISTRY OF NATURAL GAS.

With the growth of the natural gas gasoline industry natural gases have been classified into two divisions, so called "wet" and "dry" gases, depending upon whether gasoline can be commercially condensed from them. The classification is exceedingly loose because natural gas mixtures may range from those containing only methane as the combustible constituent (a gas difficult to liquify), to those in which the hydrocarbon vapors predominate and which liquify easily. Between the two extremes there are natural gases containing the different constituents methane, ethane, propane, butanes, pentanes, etc., in many different combinations. Some of these may not contain enough of the desirable gasoline constituents for commercial purposes, others may.

Natural gases not found intimately associated with oil are the so-called "dry" gases. Those found in the same strata with oil and in intimate contact with the same are those from which gasoline is obtained in the natural gas gasoline industry. The Bureau of Mines finds as the result of many analyses that natural gases are mixtures in which the hydrocarbons of the paraffin series predominate and that small quantities of nitrogen, carbon dioxide and water vapor are present. Hydrogen sulphide is sometimes present; perhaps other sulphur compounds too. F. C. Phillips found natural gases of Western Pennsylvania which he worked upon, to contain paraffin hydrocarbons, carbon dioxide and nitrogen. Other investigators invariably report at least small proportions of carbon monoxide, hydrogen and ethylene. Experimental errors in the work easily accounts for these mistakes. The authors of this paper believe the work of Ford as showing very large percentages of hydrogen to be in error. His analyses have been quoted many times in different text books. They were made in 1885. The authors of this paper in looking over the analyses made by them of thirty natural gas samples collected from all parts of the country find the heating value ranging from 685 B. t. u. to 1577 B. t. u. per cubic foot at 60° F. and 760 m.m. pressure. These analyses will be incorporated with many others in a government publication. These gases range from marsh gas, issuing from the marsh beds, and containing only methane as the combustible gas, to casing head gases that are used for lighting and heating towns. Only two of the gases, those of the highest heating value, are probably adapted for gasoline condensation. One sample contained in addition to methane, carbon dioxide and nitrogen, 75.16 per cent of ethane. The natural gas of Pittsburgh has a gross heating value of about 1177 B. t. u. per cubic foot at 0° C. and 760 m.m. pressure.

SIGNIFICANCE OF ORDINARY ANALYTICAL RESULTS.

In the analysis of natural gases by the slow combustion method, the data obtained admits of the calculation of only two of the chief constituents. The mixture, however, may contain all of the gaseous paraffin and considerable quantities of the vapors of the liquid hydrocarbons. When the lower members of the paraffin hydrocarbons predominate, the results obtained are more accurate than when the higher members predominate. Natural gases from which gasoline can be extracted contain appreciable quantities of the liquid hydrocarbon vapors. In the analysis of these mixtures the ordinary slow combustion analysis will give only approximate results for several reasons.

First—The gas mixture often contains more than two combustible constituents.

Second—Some of the gases and vapors deviate considerably from the gas laws and their true molecular volumes[1] are unknown.

Third—So small an amount of the mixture must be used in some cases that experimental errors are greatly magnified in calculating to a percentage basis.

A typical analysis of two different natural gases as is shown in Tables I and II. These contain small amounts of methane and larger amounts of ethane, propane and butane with the vapors of the liquid

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† Chemist of the Bureau of Mines.

†† Assistant Chemist of the Bureau of Mines.

[1] A government publication which covers this question is in press.

hydrocarbons pentane, hexane, etc. These analyses serve to show how approximate a combustion analysis may be even when the analysis is carefully performed.

In the analysis of gases of this type the explosion method is entirely out of the question. The analyses were made by the method of slow combustion. Duplicate analyses were made of each sample.

TABLE I—SAMPLE NO. 1.

	I. c. c.	II. c. c.
Volume of sample taken	20.00	19.95
Oxygen added	95.70	95.30
Total volume	115.70	115.25
Volume after burning	64.10	64.00
Contraction	51.60	51.25
Volume after CO_2 absorption	22.10	22.60
Carbon dioxide produced by burning	42.00	41.40

RESULTS OF ANALYSIS.

	Per Cent.	Per Cent.
Ethane	96.00	98.75
Propane	6.00	3.33
Total Paraffins	102.00	102.08

TABLE II—SAMPLE NO. 2.

	III. c. c.	IV. c. c.
Volume of sample taken	20.35	23.50
Oxygen added	96.15	126.75
Total volume	116.50	150.25
Volume after burning	60.10	85.30
Contraction	56.40	64.95
Volume after CO_2 absorption	10.40	28.20
Carbon dioxide produced by burning	49.70	57.10

RESULTS OF ANALYSIS.

	Per Cent.	Per Cent.
Ethane	65.85	66.80
Propane	37.50	36.50
Total Paraffins	103.35	103.30

The foregoing analyses show how a small difference in the contraction due to the combustion and the carbon dioxide produced will when calculated to the same basis affect the distribution of the paraffins and also the total paraffin content. The fact that the gases total over 100.0 per cent is because the correct molecular volumes of all the gases present in the mixture are not known. For example, in the case of analysis I and II (duplicate analyses) the contraction in I is 51.60 from 20.00 c.c. of the original sample while the contraction in II is 51.25 c. c. This latter result when calculated to 20.00 c.c. of sample gives a difference of 0.22 c.c. from the first, which is the experimental error.

The carbon dioxide produced in I from 20.00 c.c. of sample is 42.00 while that produced from II when calculated to 20.00 c.c. sample is 41.50 c.c. or a difference of 0.5 c.c., the experimental error.

The combined difference in the contractions and carbon dioxide change the paraffin distribution by 98.75—96.00, or 2.78 per cent in the case of ethane and 6.00—3.33 or 2.67 in the case of propane. The total paraffin hydrocarbon content is only changed 102.28—1.02.08 or 0.08 per cent.

In a like manner in the case of analyses III and IV (duplicate analyses) the contraction produced in III by the combustion is 56.40 c.c. with 20.35 c.c. of sample while the contraction produced in IV calculated to 20.35 c.c. of sample is 56.25 or a difference of 56.40—56.25 c.c. or 0.15 c.c., the experimental error.

The carbon dioxide from 20.35 c.c. of sample is 49.70 c.c. in III while the carbon dioxide in IV is 49.44 c.c. when calculated to 20.35 c.c. of sample. This is a difference of 0.26 c.c., the experimental error. Here the combined difference of the contractions and the carbon dioxide, change the paraffin distribution by 66.80—65.85 or 0.95 per cent in the case of ethane and 37.50—36.50 or 1.00 per cent in the case of propane. The total paraffin content is only changed by 103.35—103.30 or 0.05 per cent.

Although combustion analysis shows only approximately the quantity of paraffin hydrocarbons present, the total paraffin hydrocarbons are correct. The heating value and specific gravity of the gas as calculated from the analysis is also correct. The ascertaining of the different hydrocarbons that may be found in natural gases has long been a stumbling block to gas analysts. The ordinary eudiometer analysis offers nothing in the way of a complete separation. The total paraffin hydrocarbon content with only an approximation of the individual paraffins has been the only end attained. The authors in working on the problem succeeded in making a separation of a natural gas into its individual paraffin hydrocarbons by means of fractional distillation at low temperatures. Natural gas was first liquified by means of liquid air and then by means of a Töpler pump the methane was removed. The vapor pressure of liquid ethane (boiling point 93° C.) is so small at the temperature of liquid air (190° C.) that two fractionations sufficed to remove the methane, which was measured and analyzed. The residual gas was than subjected to a temperature of 130° C. and as much as could be removed was withdrawn with the pump. The mixture withdrawn proved to be ethane and propane. At 130° C. all the ethane (boiling point 93° C.) and part of the propane (boiling point 45° C.) is removed. This fraction was measured and analyzed. The residual liquid was then allowed to volatilize and found to be propane. The proportions were than found by simple calculations. Butane was not found within the experimental error of the manipulation which was perhaps .2 or .3 per cent. Traces of butane exist in the gas, however, also pentane and hexane. The complete analysis including the quantity of each paraffin hydrocarbon found by the above method follows: For comparison the ordinary eudiometric analysis of the natural gas is given. The natural gas is that used in Pittsburgh.

	By liquification and fractionation. Per Cent.	By eudiometric analysis. Per Cent.
CH_4	86.8	79.2
C_2H_6	5.7	19.6
C_3H_8	6.2	....
N_2	1.3	1.2
Total	100.0	100.0

The carbon dioxide in the Pittsburgh natural gas amounts to a trace (.03 per cent). The gas cannot be used for the commercial production of gasoline al-

though it contains sufficient of the hydrocarbon vapors to produce some condensate (drip) in the pipe lines. This is because of the immense volume of gas passing. The gas comes from West Virginia and is typical in composition of gases from that field that are supplying many towns. The natural gas from the famous Hogshooter pool of Oklahoma, some of which goes to Kansas City, contains only methane (95.4 per cent), as the combustible constituent. The rest is nitrogen and carbon dioxide. The Bureau has the composition of the natural gases that are supplying many towns. Further work is being done by the authors on the fractionation of natural gases. More difficulty is experienced in making a separation when all of the gaseous paraffins and vapors of the liquid ones are present.

OCCURRENCE OF GASOLINE IN NATURAL GAS.

The yield of gasoline from natural gas is determined largely by the quantity of the liquid paraffin vapors in the permanent gases. Temperature and pressure conditions in the well, gasoline content of the oil, and the intimateness of contact between the oil and gas, all affect the yield. Such rapid expansion of a gas from a casing head may occur as to cause a heavy condensation of vapors at the casing head.

Methane (critical temperature 95.5° C., critical pressure 735 lbs. per square inch) is always in a well in the gaseous condition. Ethane (critical temperature 35° C., critical pressure 664 lbs. per square inch) exists in some wells as a gas, in others probably as a liquid. Propane and butane are even more easily liquified than ethane. In gases used for gasoline production they are present as gases. In such cases reduced pressure is usually applied to the wells. The gasoline vapors are mixed with these permanent gases in the same manner that moisture exists with air.

In gasoline plant operation, the pressure supplied to condense the vapors must, of course, depend on the partial pressure of the vapors in the natural gas mixture. If butane (boiling point 1° C.), for instance, constitutes twenty per cent of the mixture, there would be needed a total pressure of seventy-five pounds per square inch, in order to have 15 pounds on the butane vapor, and cause condensation of the vapor to begin. For this reason one gas may produce condensate with 75 lbs., while another gas will need 200 lbs. to 300 lbs. In the standard type of cooling and pressure arrangement as used today, methane and ethane are not liquified but some propane and butane are. In addition the final mixture as received at the collecting tank will contain condensed gasoline vapors, i. e., pentanes, hexanes, etc. There will also be found a portion of the gases methane and ethane dissolved in the liquids. In other words several changes will have taken place. One has to do with the condensation of the vapor, another with the liquification of the gas and another with the solubility of the permanent gases in the liquid produced. The three changes mentioned are so intimately connected with each other that one factor cannot be disturbed without affecting the others. For instance, such a temperature and pressure could be employed as to increase the condensation of the desirable constituents (the gasoline vapors) but with increasing pressure and lowered temperature more of the undesirable gaseous constituents would liquify. These when exposed to atmospheric conditions of temperature and pressure would immediately volatilize, carrying with them some of the gasoline constituents. At increasing pressures more ethane and methane would be dissolved. With release of pressure they too would escape.

TESTING NATURAL GAS FOR GASOLINE VAPORS.

Before plant installations are made for the purpose of extracting gasoline from natural gas, a thorough investigation of the several factors should be made. These include (1) quality of gas, (2) quantity of gas, (3) disposal of product.

QUALITY OF GAS.

Laboratory methods in use at the present time consist chiefly of combustion tests, solubility tests and specific gravity tests. The combustion analysis gives only a rough approximation. The specific gravity test is much used. Natural gases may range in specific gravity from about .56 to 1.50, compared to air. Some gases are used for condensing gasoline that have as low a specific gravity as .80. All gases of this specific gravity are not adapted, however. If the carbon dioxide or nitrogen content of a natural gas is high and not known, the specific gravity test will be misleading.

Alcohol, clairoline oil, olive oil, kerosene oil, etc., all have been used for determining the solubility of natural gases. The higher members of the paraffin series are more soluble in these solvents than are the lower members. The authors have used tests that consist in shaking 100 c.c. of natural gas in 50 c.c. of alcohol or 35 c.c. of clairoline oil and noting the loss in gas volume. The test is arbitrary. Under these conditions it was found that natural gases soluble to the extent of from 30 per cent to 86.0 per cent of their volume were used for condensing gasoline. In all these tests inconsistencies have been noted, so that especially as regards the minimum specific gravity tests and solubility numbers herein given one would not feel sure about the feasibility of plant installation.

Natural gases differ much in composition. The so-called "wet" gases, for instance, might contain a very large proportion of methane, with but little ethane, propane and butane but enough of the gasoline vapors to warrant plant installation. Another gas with the same specific gravity might contain a comparatively small proportion of methane and ethane, a large proportion of butane and propane but not enough of the gasoline constituents to warrant plant installation. The safest recourse is to be had to some

type of laboratory compressor or better still to a portable outfit consisting of gas meter, gas engine, compressor, cooling coils and receiver. Such an outfit can be hauled from well to well on a wagon. Tests conducted by such a method must also be in the hands of competent persons.

QUANTITY OF GAS.

Many plants are in operation working on as little as 125,000 cu. ft. of gas per 24 hours. Some are working on as little as 40,000 cu. ft. These latter are largely experimental. A fair sized plant to handle 125,000 cu. ft. costs about $10,000. There are probably 200 plants in the United States making gasoline from natural gas.

VALUE OF RESIDUAL GASES.

Residual gases left after plant operation are of high heating value, unless contaminated with air. Air may leak into pipes due to reduced pressure in the pipe lines (as much as 25 ins. of mercury). In one case the authors found that a residual gas had a heating value almost twice as high as the heating value of the Pittsburgh natural gas. According to the facts already presented the residual gas is bound to be a rich gas, because the methane and ethane are not liquified, and only a portion of the propane and butane. Neither are all the gasoline vapors condensed. Air may appreciably lower the value of the gas, however. Some residual gases contain 40 per cent to 50 per cent of air.

DEPLETION OF THE RESIDUAL GAS AS REGARDS QUANTITY.

To give exact figures for the quantity of gas and vapor that disappear from the raw gas in plant operations is impossible. If four gallons of condensate are produced from each 1,000 cubic feet of natural gas, about 140 cubic feet of gas per 1,000 may disappear. This figure is based upon the equivalent of liquid butane, pentane, etc., in cubic feet of gas.

Tables III and IV show laboratory tests conducted on gases from two plants, at various stages of plant operation. The Bureau has many more.

TABLE III.

Lab. No.	Kind of Gas.	Gross heating value at 60° F. and 760 m. m. pressure. Calculated.	Sp. Gr. Air-1	Per cent air calculated from amount absorbed by 35 c. c. clairoline oil.	Composition Per Cent. CH_4	C_2H_6	C_3H_8	C_4H_{10}	N_2	CO_2
2281	Natural gas from Follansbee, West Virginia	2339	1.41	83.6	..	21.4	78.2	...	.4	.0[a]
2284	Residual gas after 50 lbs., compression; product has been removed	2295	1.38	82.0	..	26.6	72.8	...	.6	.0[a]
2286	Residual gas after 250 lbs., compression; product has been removed.	1913	1.15	63.6	..	77.3	22.0	...	.7	.0[a]

([a]) Trace of carbon dioxide present.

Gas is from 75 producing wells and is withdrawn under a reduced pressure of 20 inches mercury. The gasoline is blended with low grade refinery naphtha and then marketed.

DISCUSSION OF RESULTS SHOWN IN TABLE.

Table III shows the results of the analysis of the natural gas used by a plant near Follansbee, West Va. The analysis, specific gravity and clairoline absorption show this to be a rich gas. It will be seen that but little difference exists between the composition of the crude gas before and after it had been compressed to 50 lbs., per square inch. It is only after compression to 250 lbs. per square inch and cooling, that the composition of the gas mixture changes appreciably. The high heating value of the residual gas is apparent.

TABLE IV.

Lab. No.	Kind of gas.	Gross heating value of 60° F. and 760 m. m. pressure. Calculated.	Sp. Gr. Air-1	Per Cent absorbed by 35 c. c. clairoline oil.	Air calculated from oxygen.	Composition. Per Cent. CH_4	C_2H_6	C_3H_8	C_4H_{10}	N_2	CO_2	Total.
2809a	Natural Gas, McDonald, Pa....	1719	1.01	38.5	....	2.7	96.1	..	..	1.0	.2	100.0
		1204b	..	27.0	30.1	1.9	67.3	..	..	.6	.1	100.0
2807	Residual gas after 20 lbs., compression; product has been removed.	1233	..	30.2	29.0	.7	69.6	..	..	.6	.1	100.0
2809	Residual gas after 80 lbs., compression; product has been removed	1164	..	25.0	30.0	7.2	62.0	..	..	.7	.1	100.0

(a) This analysis calculated air free to show the composition of the crude gas.
(b) Actual composition of gas delivered to the compressor.

Table IV shows the results obtained from a small plant near McDonald, Pa. This is not a very "wet" gas. Its clairoline absorption number is rather low. It is probably near the low limit of a gas adapted for the condensation of gasoline. The composition of the gas does not change to a very marked degree after it has been compressed to 80 lbs. per square inch.

SOME OBSERVATIONS ON BASE METAL THERMOCOUPLES.*

By O. L. KOWALKE.

The thermocouple as a means of measuring temperatures seems to be used by a large variety of industries, if one may judge from the records of sales. It is peculiarly adapted for this purpose because of (1) the small volume the junction occupies, (2) the robust nature of the couple itself as compared to a thermometer, (3) the simplicity of the measuring or indicating instruments, (4) the rapidity with which the measurement can be made. Up to about seven years ago the platinum couple, which had been thoroughly investigated and tried out, was almost alone in the field. Since then there have appeared on the market couples made of the baser metals, such as iron, nickel-chromium, nickel, cobalt and other alloys. These couples came into favor because of their cheapness as compared to the platinum couple both as to first cost of the outfit and the cost of renewals of the couple itself, the high electromotive force generated and the use of a robust double-pivoted millivoltmeter. Among the causes for the inaccuracy of the platinum couple were heterogeneity of the wires in the couple and their contamination by metals or gases from the place where the temperatures were to be measured. All but the first of the causes named can be avoided after the couple is made, but the wire must be made homogeneous before the couple is completed.

Since the voltage generated by the couple for a given temperature is the summation of all the electromotive forces due to the contact of two dissimilar metal portions, it can really be seen that it is imperative that the metal be as homogeneous as possible if the electromotive force indicated be that resulting from the two metals at the hot junction. If, then, the couple is composed of metal which is not homogeneous, then at each junction of two dissimilar metals there will be set up a voltage which is a function of the temperature existing at that point. Should the position of the couple be changed with respect to its depth of immersion, then the resulting voltage will be changed even though the temperature had not changed at all. A couple made of wires which are perfectly homogeneous is apt to be rather expensive, and the only combination which seems to fulfill this condition is the platinum and platinum-rhodium couple.

It is possible to get a couple which is sufficiently homogeneous so that the indications are satisfactory for many commercial purposes where an accuracy of about 25 to 50° is wanted. This condition is realized in the combinations of which base metal couples are made. Not all of the couples meet this condition with the same accuracy, and not all of the couples retain their original accuracy. Some couples appear to change or deteriorate with use more than others, due to oxidation, crystallization, segregation of the metal and other undetermined causes.

It was the purpose of this investigation to determine how electromotive forces of couples varied with the temperature, and how constant this force remained with excessive heatings and coolings, and also when exposed to various temperatures for extended periods of time.

PROCEDURE.

Couples were purchased from five of the prominent makers, and were cut to lengths of about 18 ins. To each couple about 3 ft. of flexible lamp cord was soldered, and the wires at the point of soldering and all other required points were carefully insulated from each other.

The couples under test were all compared with a platinum and platinum-rhodium couple No. 3P, which had been standardized against a similar couple, "B. S. No. 120," certified to by the Bureau of Standards. The latter couple had not been used since it came from the Bureau of Standards, and was used only to standardize couple No. 3P at the beginning and at the end of the series of tests.

Couple No. 3P changed slightly during the investigation, and a correction was made for the indications of each series of tests. It was assumed that the change was a progressive one, and the total error divided into equal parts and the proper correction made in the corresponding chronological series.

All couples were calibrated over the range given by the manufacturers in their catalogues, and only one base metal couple at a time was compared with the platinum couple No. 3P.

Series 1. All couples were first calibrated against No. 3P with a length of about four inches heated.

Series 2. All couples were again calibrated, but with a length of about 15 inches heated to determine the effect and presence of heterogeneity in the wires.

Series 3. All the couples were now subjected at one time to a constant temperature of 400° C. for a period of about twenty hours. After this treatment each couple was again separately calibrated with a length of 15 inches heated.

Series 4. A second treatment consisted in heating all of the couples together at a constant temperature of about 600° C. for a period of twenty-four hours. After this treatment each couple was calibrated separately, the idea being to determine the effect of heat treatment at 600° C. over that at 400° C.

Series 5. All the couples were now heated together for a period of twenty-four hours at a temperature of 800° C., and afterwards separately calibrated as before.

The calibrations and heat treatments as indicated in Series 3, 4 and 5 were made with each of the base metal couples heated for 15 ins. of its length.

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FURNACES.

Electrically heated tube furnaces were used in all of the tests. One furnace was 10 ins. long, and the other was 20 ins. long, each having a tube about one inch internal diameter, and were used for the calibration at 4 ins. and 15 ins. depth of immersion, respectively. A tube furnace about 2½ ins. in diameter and 24 ins. long, so that all should be treated together, was used for the heat treatments at the temperatures of 400°, 600° and 800° C. The current on the furnace was controlled by means of a bank of incandescent lamps, and could be adjusted so that the temperature remained stationary for an indefinite period.

METHODS OF MEASUREMENT.

All measurements were made on Leeds & Northrup Type K potentiometers, and only one base metal couple at a time was compared with the standard platinum couple, and the voltage of each couple was determined by a separate potentiometer, the standard cells for each potentiometer being checked for accuracy.

Asbestos discs slightly less than the diameter of the tube, perforated in the center, were slipped on each couple and served to keep the couples centered in the furnace. The two couples were then introduced into the furnace so that the junctions of the couples met. The temperature of the furnace was then raised to about 300° C. for the first point so that a good reading on the platinum couple could be obtained. From this point up the temperature was increased by intervals of about 100° C. At each point the temperature was maintained stationary so that constant readings on both couples were obtained for a period of about two minutes. Thus all lag in the indications of the couples was avoided. During the entire procedure the cold junctions of both couples were kept at zero degrees Centigrade by surrounding them with a bath of melting ice, care being taken to avoid a circulation of air about the cold junction.

COUPLES USED.

The base metal couples used in this investigation are designated as follows:

Couple No. 6A, composed of wires ⅛ inch square and covered throughout the length, excepting about 2 inches, with a winding of asbestos cord, over which there was applied a solution, presumably sodium silicate. This couple had for its negative element an alloy of nickel and chromium, and the positive element one of nickel and iron.

Couple No. 7A was made of No. 8 B. & S. gauge wires, the negative element being composed of nickel with a small amount of aluminum, and the other element a nickel-iron alloy. This couple was purchased with both wires bare, and for the purpose of test an asbestos sleeve was drawn over one of the wires.

Couple No. 18 was composed of two No. 10 B. & S. gauge wires, each of which was wrapped with asbestos thread and painted over with carborundum paint. The negative element was made of nickel with a small amount of aluminum, and the positive element of iron with a small amount of nickel.

Couple No. 19, composed of two No. 10 B. & S. gauge wires, one of which was covered with an asbestos sleeve over which there was a coating of carborundum paint. The negative element consisted of nickel containing a small amount of iron, and the positive element contained iron with a small amount of nickel.

Couple No. 20 was made of two No. 16 B. & S. gauge wires, one of which was covered with an asbestos sleeve, and then a coarse asbestos cord was wrapped around both of the wires. No paint covering of any sort was used apparently on this couple. The negative element was a nickel-copper alloy, and the positive element an iron-manganese alloy.

OBSERVATIONS.

The results of the tests on couple No. 6A appear to show that this couple is resistant to oxidation, and was in about as good condition at the end as in the beginning of the series of tests. The asbestos covering appeared to be the most robust and satisfactory

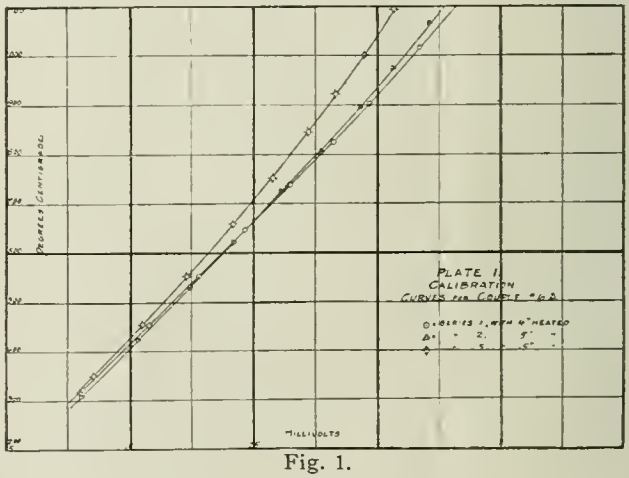


Fig. 1.

of the entire lot. The data of Tables I to V and the curve in Plate 1 show that there is a slight lack of homogeneity in the couple as evidenced by the variation in calibration with 4 inches and 15 inches, respectively, of the couple heated, the difference being about 25° at 40 millivolts. The treatments at 400° and 600° C. had little effect upon the calibration of the couple. The treatment at 800° C. had, however, a marked effect upon the calibration, throwing the curve up so that at 35 millivolts the difference between the indications of the initial and final calibrations was nearly 125° C. This large difference is due apparently to some marked change in the structure of one of the wires composing the couple.

The data and curves for couple No. 7A are shown in Tables I to V and Plate 2. From Plate 2 it is apparent that the calibration curves of this couple are far from being a straight line. The calibrations with 4 inches and 15 inches, respectively, of the couple immersed in the furnace coincide very closely up to 600° C. Above this point the curves separate

so that at about 24 millivolts there is a difference of 25 degrees in the indications of the temperature, thus showing the effect of heterogeneity of the wires upon the indication of the couple. It is interesting, however, to note that the heat treatments at 400°, 600° and 800° C., respectively, had very little effect upon

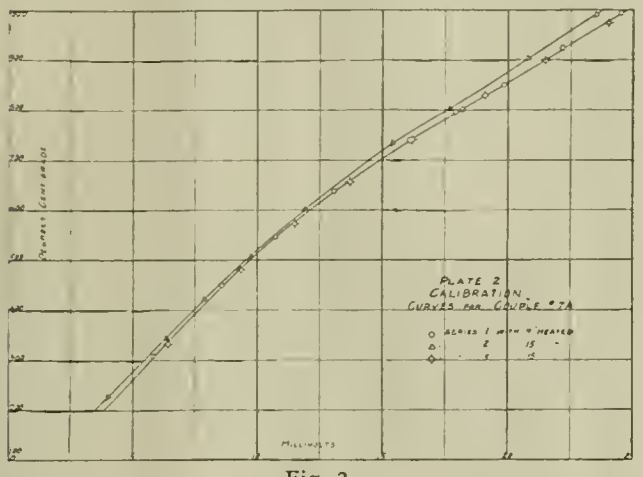


Fig. 2.

the constancy with which this couple would indicate the temperature. This couple is robust, and stood the prolonged heat treatments and calibrations without any signs of damage; even the asbestos covering appeared to be in good condition.

Couple No. 18 had a lower electromotive force than either of the two preceding ones. It was found that the iron wire in the couple started to oxidize during the second calibrations. As a result of the heat treatment at 400° C. and the third calibration, one of the wires was badly swollen, and after the treatment at

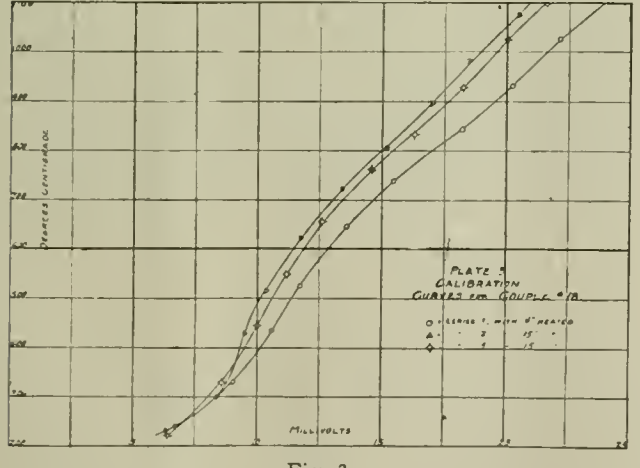


Fig. 3.

800° it was oxidized so completely that it broke during the subsequent calibration. An examination of the wire revealed the fact that it was oxidized for a distance of about 6 inches beyond the hot junction. It seems likely that the metal of this wire had combined with the silicon of the carborundum paint and formed ferrosilicon. The other wire and its covering were in very good condition with the exception of the carborundum paint, which peeled badly during the first calibration. The data and curves for this couple are shown in Tables I to V and Plate 3. Inspection of Plate 3 will show that for an electromotive force of 20 millivolts there is an apparent difference in indication of the temperature by about 130° for a depth of immersion of 4 inches and 15 inches, respectively. This difference is due, no doubt, to a lack of homogeneity of the wires and certain recalescent

TABLE I.—DATA OF SERIES 1. FIRST CALIBRATION. COUPLE 4 IN. IN FURNACE.

Couple No. 6A.		Couple No. 7A.		Couple No. 18.		Couple No. 19.		Couple No. 20.	
C°	M. V.	C°	M. V.	C°	M. V.	C°	M. V.	C°	M. V.
324	11.39	316	5.86	240	6.75	360	8.41	318	15.70
454	16.64	450	8.59	330	9.09	452	10.40	445	22.51
554	20.73	545	10.76	435	10.66	542	12.45	540	27.66
646	24.41	636	13.10	525	11.75	643	14.98	634	32.99
737	28.03	738	16.12	645	13.64	749	17.34	721	38.11
825	31.51	800	18.27	738	15.49	836	20.65	825	44.85
906	34.36	924	22.21	843	18.20	931	23.60	896	49.41
1018	38.45	993	24.52	933	20.28	1022	26.57	997	55.02
1115	41.43			1026	22.19	1107	29.58		
				1109	24.16				

TABLE II.—DATA OF SERIES 2. CALIBRATION WITH 4 IN. OF COUPLES HEATED.

Couple No. 6A.		Couple No. 7A.		Couple No. 18.		Couple No. 19.		Couple No. 20.	
C°	M. V.	C°	M. V.	C°	M. V.	C°	M. V.	C°	M. V.
310	11.20	226	3.99	230	6.32	304	7.39	245	11.99
425	15.72	337	6.40	325	8.34	436	10.12	352	17.97
532	19.91	421	7.88	428	9.49	531	12.29	441	22.75
621	23.43	518	9.75	516	10.38	600	14.04	530	27.62
725	27.30	628	12.42	621	11.76	715	17.21	653	34.67
808	30.55	733	15.40	723	13.43	815	20.17	700	37.66
897	33.67	806	17.72	805	15.23	906	23.13	783	42.85
975	36.30	906	20.81	895	17.05	994	25.84	893	49.84
1067	39.19	987	23.47	981	18.51	1078	28.81	984	55.17
				1072	20.46				
				1174	22.77				

TABLE III.—DATA OF SERIES 3. CALIBRATIONS AFTER TREATMENT AT 400° C., WITH 15 IN. HEATED.

Couple No. 6A.		Couple No. 7A.		Couple No. 18.		Couple No. 19.		Couple No. 20.	
C°	M. V.	C°	M. V.	C°	M. V.	C°	M. V.	C°	M. V.
324	11.81	315	6.02	218	6.33	321	7.88	323	16.55
429	16.05	440	8.28	346	8.79	441	10.36	445	23.10
534	20.42	540	10.49	436	9.81	528	12.36	543	28.52
618	23.56	621	12.47	520	10.87	639	15.25	634	33.87
723	27.26	709	15.22	628	12.27	719	17.56	724	39.11
808	30.45	808	18.47	713	13.86	825	20.59	815	45.19
912	33.97	895	21.34	825	16.43	900	23.10	900	50.66
991	36.63	993	24.81	900	18.20	998	26.37	997	56.54
1090	39.53			990	19.82	1085	29.37		
				1080	21.48				

TABLE IV.—DATA OF SERIES 4. CALIBRATIONS AFTER TREATMENT AT 600° C., WITH 15 IN. HEATED.

Couple No. 6A.		Couple No. 7A.		Couple No. 18.		Couple No. 19.		Couple No. 20.	
C°	M. V.	C°	M. V.	C°	M. V.	C°	M. V.	C°	M. V.
343	12.71	355	7.08	213	6.04	355	8.91	316	16.38
454	17.09	436	8.68	358	9.32	450	10.83	429	22.30
546	20.76	545	11.04	471	10.32	555	13.33	546	28.83
657	24.80	642	13.41	540	11.05	650	15.80	637	33.83
758	28.66	739	16.17	635	12.21	746	18.31	736	39.77
834	31.36	819	18.64	729	13.82	843	21.64	810	44.75
921	34.33	917	21.69	834	16.14	911	23.85	894	50.16
1006	37.09	995	24.37	912	17.71	1013	27.32	985	55.25
1110	40.29			993	19.12	1096	30.19		
				1102	21.13				

TABLE V.—DATA OF SERIES 5. CALIBRATIONS AFTER TREATMENT AT 800° C., WITH 15 IN. HEATED.

Couple No. 6A.		Couple No. 7A.		Couple No. 18.		Couple No. 19.		Couple No. 20.	
C°	M. V.	C°	M. V.	C°	M. V.	C°	M. V.	C°	M. V.
350	12.20	332	6.47	222	6.42	246	6.35	324	16.88
455	16.12	476	9.31	330	8.61	365	9.02	459	24.12
553	19.78	571	11.51	446	9.96	465	11.38	563	29.40
658	23.40	654	13.73	554	11.18	562	13.61	645	34.59
752	26.61	740	16.19	655	12.61	662	16.30	735	40.09
845	29.49	827	19.12	763	14.65	750	18.88	835	46.93
922	31.72	900	21.53	838	16.31	854	22.22	928	52.70
1004	34.03	974	24.07	927	18.25	930	24.71	980	54.77
1095	36.10			1025	20.08	1020	27.05		
				1099	21.58	1102	30.83		

effects. The calibration curve after the treatment at 400° C. falls between the first and the second calibration curves, showing that some of the heterogeneity has been partially removed. The calibration curves resulting from the treatments at 600° and 800° C. are thrown between the curve after the treatment at 400° and the first calibration with 15 inches of the couple immersed. It is also apparent that at 9 millivolts there is a point of a marked inflection and that the slope of the curve at this voltage is different for all the curves. Thus it would seem that there would

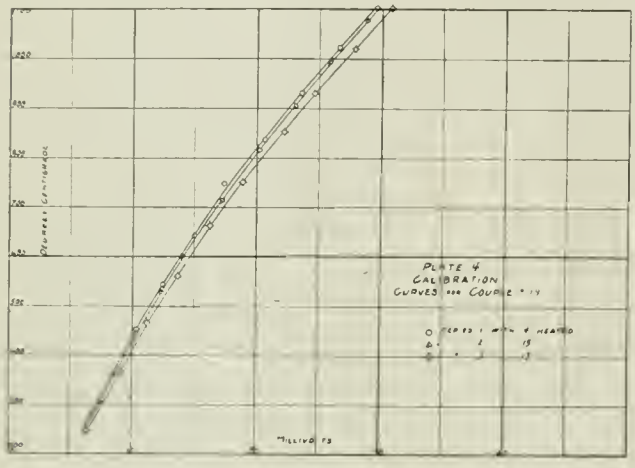


Fig. 4.

be considerable difficulty in arranging a proper scale for the indicating instrument supplied with this couple.

Couple No. 19 showed very robust qualities, the metal being in fine shape at the end of the series of tests. The asbestos sleeve with which one wire was covered had been completely destroyed. The data and curves in Tables I to V and Plate 4, respectively, show a gradual change in the calibration after each treatment, amounting to about 10 degrees at the higher temperature. The couple appears to be homogeneous, as there is only a slight difference in the calibration curves for a depth of immersion of 4 inches and 15 inches. The curve is very nearly a straight line. The discrepancy between the first and last calibrations is about 40° at 30 millivolts.

The data and curves of couple No. 20 in Tables I to V and Plate 5 show that the variation of millivolts with temperature is almost linear. This couple gives a higher electromotive force for a given temperature than any of the other couples. It is, however, less resistant to oxidation. This may be due to the fact that the wires composing the couple are only about one-half the diameter of the other couples. After the treatment at 800° C. one of the wires had been oxidized so that it was only about one-half its original size, while the other wire had swollen to about twice its normal size. Both wires had become very brittle and crystalline to within 6 ins. of the cold junction. At the end of the last calibration one of the wires broke in two and spoiled the couple. The asbestos covering on this couple remained in fair shape during the entire series of tests. The calibration curves for 4 ins. and 15 ins. immersion show a slight variation in voltage for a given temperature, indicating that the couple is somewhat heterogeneous. This difference in temperature for a given voltage is less than 20°, which is doing very well for a couple made of this sort of material. The heat treatments at 400°, 600° and 800° C. did not seem to have very much effect upon the change in calibration. This difference is so small that it compares favorably with the changes which frequently take place in high-grade platinum couples.

CONCLUSIONS.

This series of investigations seem to point to the fact that it is possible to obtain a base metal couple which is reasonably homogeneous and will give indications of temperature which are sufficiently constant to meet the needs of perhaps the greatest number of requirements for high temperature measurements in the industries.

There are some instances where the temperature is to be known to an accuracy better than 25°, and for such requirements it would be necessary to use a higher grade of equipment, and, furthermore, for such requirements it will be necessary to make frequent calibrations.

It would seem reasonable that the makers of thermocouples determine from the purchaser the particular conditions under which the couple is to be used and that the calibration of this couple be made for the same length of immersion at which the purchaser is going to use it.

A couple which will indicate an apparent difference of temperature amounting to about 130° C. when immersed at different lengths in the bath or furnace is not giving the service that ought to be rendered.

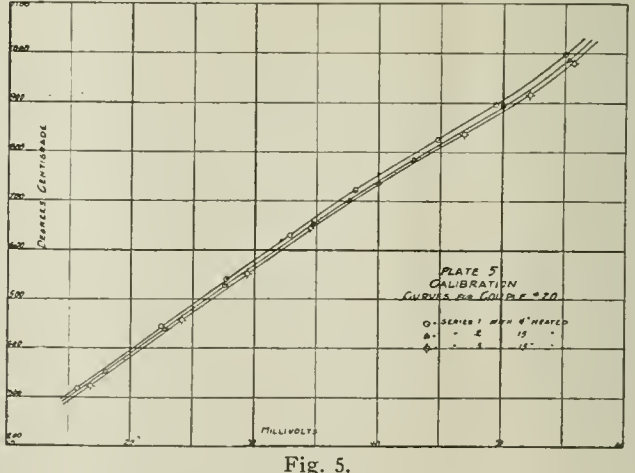


Fig. 5.

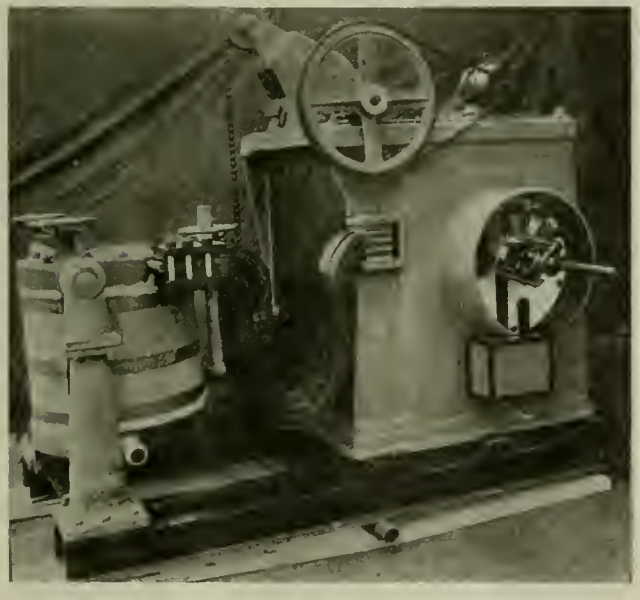
From these tests it appears that not all manufacturers are careful in sending out couples which have been thoroughly annealed to remove all stains resulting from mechanical treatment. Once the couple has attained its permanent structure, there does not seem to be much change in the electromotive force.

THE PLANT.

GERMAN CRUCIBLE ELECTRIC FURNACES OF TRANSFORMER TYPE.

By FRANK C. PERKINS.

The accompanying illustrations show novel and interesting electric transformer crucible furnaces designed at the plant of the engineer Hugo Helberger for melting metals such as tin, zinc, lead, brass, copper, nickel, silver, gold, platinum, iron and steel as well as for melting glass and enamel. The melting takes place in ordinary graphite or charcoal melting crucibles which are prepared by a special process.



Method of Charging Crucibles.

This German crucible-furnace consists of an alternating current transformer for any voltage, with holding mechanisms cooled with water for the crucible directly connected with it, and provided with carbon contacts. The transformer and furnace thus form one apparatus connected together; to control the melting process the furnace is provided with an ampere meter and a regulating switch for connection with an alternating current circuit.

In operating the furnace the melting vessel is first placed with the holding mechanism screwed firmly with a hand wheel. The door of fire clay is closed and a small current switched on with the regulating switch. The upper holding mechanism covers the melting vessel only at the edge so that its contents can be conveniently observed; this opening also serves for filling the vessel with material to be melted and allow the content to be stirred.

After a few minutes of connection with the current the vessel glows and the contents melt. All this takes place before the eyes of those attending to the apparatus, without their being in the least annoyed by radiation of heat or other unpleasantness. The melting process can thus be exactly observed and the exact moment can be noted when the melting is complete so that at the proper moment additions can be put into the fusion without disturbing the process.

As to working expenses, it is said that in recent tests pure copper yielded the following results. There were 16.5 kilograms of copper melted in 396 kilowatt minutes and 18.5 kilograms were melted in 420, and 20 were melted in 450 kilowatt minutes, a total of 130 kilograms of pure copper melted in 2900 kilowatt minutes. Taking 5 pfg. (about $.012) as cost of current per kilowatt hour, the melting of 1 kilogram of pure copper costs about 1.85 pfg. (about $.025).

In the melting of precious metals, 1 kilo gold of 14 carats required 30 kilowatt minutes = 2.5 pfg. ($.006) and 1 kilo pure platinum required 615 kilowatt minutes = 50 pfg. ($.125) to melt.

It is pointed out that the melting of small quantities is less favorable than of large ones, and the working expenses for melting 100 kilo are relatively much less than those here given for comparatively small quantities.

It is claimed that these examples afford proof that the electric crucible in the Heldberger furnace can compete with any other kind of firing for melting without taking the other great advantages into account which are connected with melting by electricity.

It is held that the transformer crucible electric furnace can be set up in any place, even where there is a wooden floor and it is not necessary for a chimney to be present. The melting takes place directly under the eyes of the furnace attendants, without their being annoyed by radiation of heat. It is maintained that the management of the furnace is exceedingly simple, as any degree of heat can be adjusted with only a change of circuit. The ease of regulating renders the melting of precious metals possible without any loss. Temperatures of more than 3000° C. can be attained.

In regard to the safety in working and durability it is held that as in these furnaces there are no complicated parts; they are durable and safe in working and those parts which are liable to wear and tear are

easily changed, while the wearing away of the transformer itself does not take place.

The melting vessels used are ordinary graphite or carbon crucibles, but are prepared according to a special process before use. The preparation is exceedingly simple, requiring no special appliance, so that it creates no difficulty in using the furnace.

The smallest crucible furnace has a melting capacity in kilogram copper of 0.5 with 3 kilowatt maximum for transformer the weight in kilograms being about 200 for this furnace. A furnace for melting 10 to 30 kilograms of copper has a 30 kilowatt transformer, while a furnace for melting 20 to 60 kilograms has 50 kilowatt transformer.

It is said that the melting capacity depends on the kind of material for melting. In a furnace in which 3 kilos copper can be melted, but only 1 kilo platinum can be melted and a furnace sufficient for 10 kilos copper would only be suitably employed to melt 5 kilos pure iron.

In order to calculate the time and amount of current used detailed time experiments are being carried out at present with every kind of metal but it will serve for the present to state that on an average 100 kilo of iron require 75 kilowatt hours and 100 kilo of copper require 37 kilowatt hours while 1 kilo of platinum requires 10 kilowatt hours.

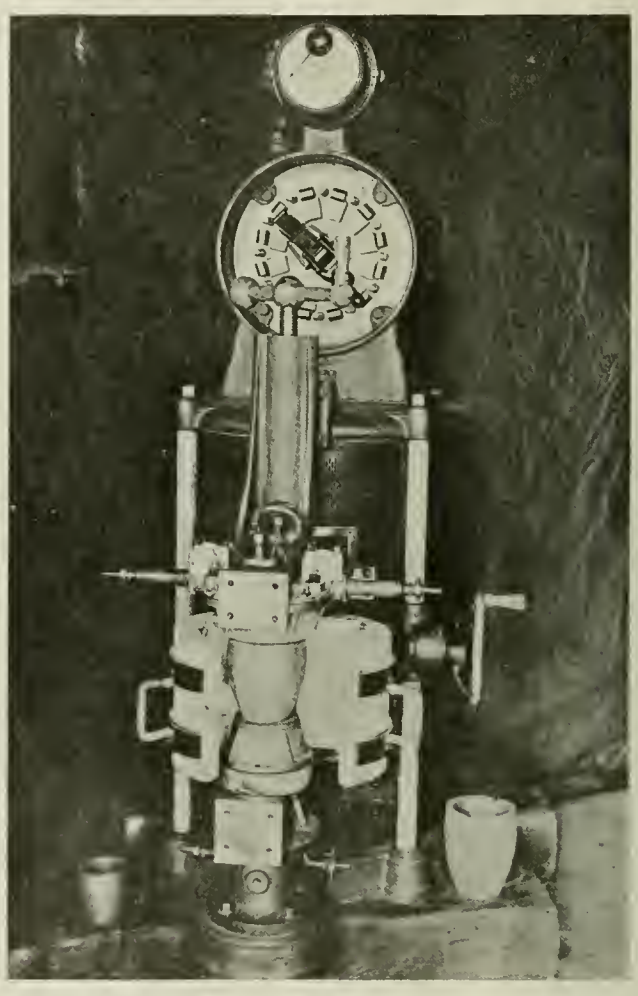
The statement above mentioned as to the transformer used and as to current required are the maximum strengths of current with which each may be charged. Each transformer is provided with regulating apparatus for 12 degrees, and this regulation is carried out by changing the winding relations of the primary and secondary coils so that no loss of current results from regulation. According to the kind of material for melting, the proper degree of current can be chosen, and the furnace attendants can measure out the proper degree of heat for the material by a simple manipulation at the proper moment.

Some most interesting experiments were made with these transformer crucible furnaces by Dr. Ludwig Weiss, who wrote a detailed report for the *Electrochemische Zeitung*. He states that with Prof. Muthmann he was testing various kinds of electric heaters and employed many kinds of furnaces. The furnaces in the trade frequently did not attain the desired temperature, or the vessel to be heated was too small, or the durability and simplicity of the heaters as well as the attendance on them left much to be desired.

The principle of construction is certainly not new, as it is that of electrical resistance. But the uncommon construction, the rapid and certain manner of working, also the circumstance that on working with this furnace one is not at all annoyed by heat, smoke, or soot, but can continually watch the melting process, is of great value.

It is stated that first the temperature measurements were taken with a pyrometer "Fery" on two different large furnaces and showed that the prevailing temperature inside the crucible was about 200-300° higher than on its outer side. This showed an essentially better utilization of the heat conveyed and the crucible was also better preserved than in the case of using coke or gas. The crucibles used therefore lasted much longer and stood three to five times the number of meltings.

The rise of temperature takes place very rapidly. A common graphite crucible 8 cm. in height was heated within 11 minutes 1495°, on employing firstly 40, lastly 100 amperes and 110 volts. A large carbon



View Showing View of Furnace of 100-Kg. Capacity.

crucible 18 cm. in height, 2.5 cm. in thickness and 12 cm. inner width was heated for 33 minutes and at the beginning the current strength was 50 and finally 275 amperes and 92 volts. The temperatures of this crucible rose in 3 minutes to 1350°, in 12 minutes to 2020°, in 24 minutes to 2190°, and in 33 minutes to 2300°. The rise of temperature was not ended with this.

About 400 grammes of the finest quartz sand was put into the crucible. In 5 minutes this had become soft and in 3 minutes more it could be drawn out into long filaments which agreed entirely with the so-called English quartz glass. What remained in the crucible has become almost transparent, in some

places quite clear and without enclosing bubbles. The experiment had finally to be stopped as the crucible had suffered much waste.

In order to prevent this the crucible which was 18 cm. high, was surrounded with a jacket of fire clay, and the intervening space filled with quartz powder. The outer fire clay case was finally made as air-tight as possible, with asbestos and fire clay mortar. Under these circumstances a much higher temperature was reached than before. After 8 minutes the temperature was 1000°, 90 amperes 104 volts, and after 20 minutes the temperature was 1760° 160 amperes 101 volts, while after 35 minutes the temperature was 2510° 235 amperes and 65 volts, and after 45 minutes the temperature was 2715° 258 amperes and 93 volts. It is stated that the last temperature measurement is too low, as the pointer of the milli-voltmeter employed rose over the scale.

Then a series of resistance of 71 ohms was inserted into the circuit, on which the voltage shown on the millivoltmeter went back to approximately one half of the former amount. For some time longer a rise of temperature could be ascertained, if it was not measured, and at the end, with 290 amperes and 88 volts, the temperature attained rose to over 3000°.

Later quartz was put into the crucible and after a short time filaments of melted quartz could be drawn out of the crucible. Finally, the whole contents of the crucible were taken out and moulded between previously heated steel plates in a press to a disc about 1 cm. thick and 10 cm. broad. The quartz had in some places become quite as clear as water. After finishing the experiment (after 3 hours) the carbon crucible showed only quite a small wasting. The exterior insulating bed or quartz was on the contrary completely melted away.

It is said that further experiments in this direction as to the use of suitable insulating material, are still in progress. There is no difficulty in melting silver, copper or gold; one kilo of copper is melted in 4 minutes and the graphite used was put into the furnace in a cold state.

Steel and wrought iron, also nickel, can be rendered quite fluid in a very short time and cast. It is remarkable that the melting of metals can be carried out almost without any waste, as in consequence of the easy regulating of the oven and the ready observation of the melting process, overheating can be completely cut out.

It is claimed that as temperatures of far over 2000° are easily reached, it goes without saying that platinum and metals difficult to melt can be melted. Glass and enamel can be melted in graphite crucibles which are covered with fire clay, be directly melted from their ingredients.

The possibility of working a larger number of furnaces parallel and independent of each other, the easy filling of the crucibles, the possibility of watching the melting continually, of making additions, the rapidity of the work, the great safety in working and durability of the furnaces will secure for them a large scope of usefulness.

These electric transformer crucible furnaces have been introduced into brass and bronze foundries and into smaller iron and steel foundries and are used for melting platinum and iridium in the ceramic and glass industries. The freedom from smoke and soot and the independence of chimneys, allow them to be put up in any place desired without danger.

OSMIUM-PLATINUM—A NEW ALLOY.*

By F. ZIMMERMANN.

Of the several metals of the platinum group, platinum, palladium, iridium and rhodium have been most generally employed in the industrial arts, either alone or in combination as bivalent alloys. Of the latter, iridium-platinum is the best known, but the growing scarcity of iridium has led to the search for other combinations of the metals of this group yielding alloys possessing physical and chemical properties of equal if not greater value. The rarer metals of the platinum group are not easily obtained in great purity, and because of this fact but little success has heretofore been obtained when combining them as bivalent alloys. Furthermore, the strong affinity of osmium for oxygen has increased the difficulty of making alloys of it with other metals in definite proportions. After much experimentation by the author, highly refined platinum and osmium have been successfully combined in widely varying proportions yielding alloys of commercial value. While the two metals may be combined in almost any proportion, alloys containing from 1 to 10 per cent of osmium and 90 to 90 per cent of platinum are chiefly used.

Great purity of the components is essential, as the presence of small percentages of other elements appears to be very detrimental to the properties of the resulting alloy. According to the chemical and physical behavior, it seems that one part of osmium in an alloy with platinum will take the place of two and one-half times its weight of iridium. The osmium-platinum alloy is very acid-resisting, and for this reason may be of great service in the electrochemical industry. Its electrical resistance is considerably higher than that of an iridium-platinum alloy of the same percentage composition. The alloy further possesses great hardness and tensile strength. Wires of the finest size are drawn with comparative ease.

A thorough study of the alloy is in progress, and definite results of tests may be of sufficient interest for a later paper.

The alloy has been patented—U. S. Patent No. 1,055,109, of March 4, 1913.

* Paper presented at the 24th General Meeting of the American Electrochemical Society, at Denver, Colo., Sept. 9-11, 1913.

THE ELECTRIC ZINC FURNACE.*

By PETER E. PETERSON.

From the nature of the present retort method of recovering zinc from zinc concentrates it is almost impossible to conceive of any improvement therein that would lead to increased capacity and decreased costs, let alone the possible recovery of zinc from the abundant complex zinc ores (containing copper, gold, silver, lead and iron) at a reasonable cost and appreciable recovery of the other metals.

The metallurgy of zinc is one of distillation. The zinc must be vaporized at a high temperature and in a reducing atmosphere. Outside of the retorts the electric furnace is the only smelting device that can meet these conditions.

The electric furnace at present seems to hold out

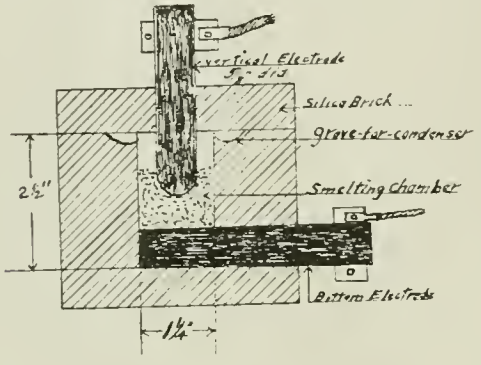


Fig. 1.

the only hope for improvement in zinc smelting.

The possible apparent advantages are: Large units, continuous feed and discharge, and the recovery of gold, silver, copper and lead in the form of copper matte or lead bullion.

The problems encountered in building a furnace to make the above advantages a reality have been many, and perhaps much time and work can be saved to others by a discussion of different types of furnaces employed.

THE FIRST FURNACE.

Fig. 1 shows a vertical section of the first furnace experimented with. This small furnace had no opening to the outside, although there was some leakage of gas around the upper electrode.

The charge consisted of a mixture of zinc sulphide, copper sulphide, lead sulphide and iron sulphide, and sufficient metallic iron to desulphurize the zinc sulphide ($ZnS+Fe=Zn+FeS$).

The furnace was connected to a small direct-current generator and run at the rate of 4 kw., the amperes varying from 40 to 50.

There was no way of telling when the charge was smelted, so a series of runs was made ranging from one to three hours. At the end of three hours the charge was completely smelted. The resulting matte showed from 1 to 2 per cent Zn and small shots of metallic lead, while 95 per cent of zinc in the charge was recovered in form of a high-grade spelter assaying 99.8 per cent zinc.

The three-hour run was repeated, and practically the same results obtained.

Another furnace was built with a condensing chamber on one side with a small opening for escape of gases. With this furnace it was not possible to condense the zinc to spelter, it being condensed in the form of blue powder.

LARGER FURNACE BUILT.

Results with these small furnaces were so encouraging (and there seemed to be no difficulties in condensing the zinc) that a larger furnace was built along the same lines. This furnace was constructed of ordinary fire brick, having walls 1 ft. thick and a smelting chamber 1 ft. square and 2 ft. high. The top consisted of slabs of fire brick 2 ins. thick, with a charge hole and an opening for the electrode. The bottom electrode was a block of iron having a cross-section of 1 in. by 12 ins. extending through the wall and protruding 8 ins. The vertical electrode was a carbon rod 2 ins. in diameter and 4 ft. long. This furnace had a rectangular condensing chamber 6 ins. by 6 ins. by 12 ins., with a baffle running the long way, causing the gases to circulate first down one side and then up the other. There was a small opening ½ in. (1.3 cm.) in diameter at one side of the condenser for the escape of gases. (See Fig. 2.)

The furnace charge used consisted of unroasted zinc concentrate analyzing as follows: 47.81 per cent Zn, 9.21 per cent insoluble, 6.2 per cent Fe, 1.5 per cent Mn, 30.32 per cent S, 1.4 per cent Cu, 0.035 oz. Au, and 12.2 oz. Ag. Scrap iron was added to desulphurize the zinc.

The power was obtained from a 50 kw. transformer. The electrodes were connected to a 100-volt circuit, and in series with the circuit was placed a choke coil to protect the transformers in case of short circuit and at the same time to somewhat regulate the current.

Numerous runs varying from four to twelve hours were made. The condensing arrangement failed to condense anything but blue powder. The furnace was found hard to regulate. The power consumption was irregular, and consequently the heat was the same. Attempts were made to tap the furnace, but were not very successful, although some slag and matte was tapped which analyzed as follows: Slag: Zn 0.4 per cent, Cu 0.19 per cent, FeO 11.1 per cent, Mn 0.6 per cent, SiO_2 64.65 per cent, Au trace, Ag 0.35 oz. Matte: Zn 1.3 per cent, Fe 60.4 per cent, S 29.35 per cent, Cu 1.70 per cent, Au 0.03 oz., Ag 9.4 oz. The analysis of the slag and matte is interesting and showed the possibilities of the process.

CHANGE IN CONDENSERS.

The furnace was next equipped with a 2-in. (5 cm.) iron pipe 2 ft. (60 cm.) long for a condenser. This pipe was flush with the inside, and stuck out a

*Paper presented at the 24th General Meeting of the American Electrochemical Society, at Denver, Col., Sept. 11, 1913.

foot into the air. With this arrangement it was possible to condense some spelter after an hour's run, which allowed time to heat the condenser up to the condensing temperature. At this stage of the experimenting it was evident that for successful condensation of volatized zinc to spelter there must be some way of controlling the temperature. The next experiment consisted of a 2-in. (5 cm.) iron pipe 6 ft. (180 cm.) long extending across the top of the inside of the furnace, with series of holes bored into the upper side of pipe for the admission of zinc vapors, the theory of the apparatus being that with a long pipe, one end cold, the other hot, between these two temperature extremes there would always be a zone of the proper condensing temperature.

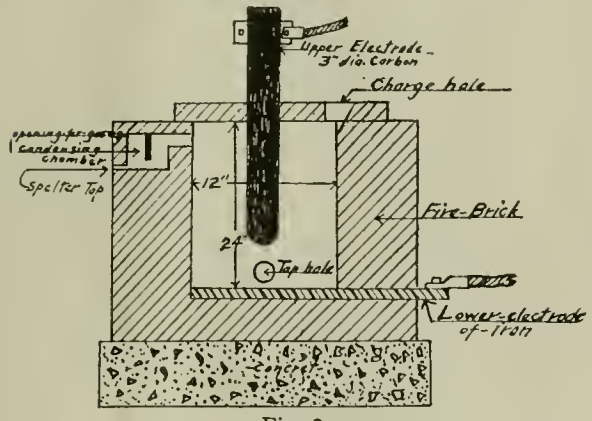


Fig. 2.

This condenser gave fair results. Starting the furnace cold, at the end of an hour it was noticed that condensing commenced, and would continue at a good efficiency for an hour, when the condenser seemed to get too hot, or rather, the zone of proper condensing temperature was greatly reduced in area. Various means were tried to increase the length of this condensing zone.

A large pipe 8 ins. (20 cm.) in diameter was inclosed with brick and heated with coal. Clay tubes of varying lengths and thickness were tried. Iron pipe insulated with varying thickness of asbestos and chambers of varying dimensions in the wall of the furnace were experimented with, but none of these gave better results than the 2-in. pipe 6 ft. long.

The problem seemed to resolve itself into three parts, that is, a certain temperature was found to be necessary as well as a certain area, and that this area must not be too far away from the source of distillation. In other words, the zinc must not be kept in vapor form too long before condensing. The furnace seemed to stand up well, except the cover, which usually did not last more than a couple of days.

FURTHER DEVELOPMENT.

The bottom electrode, although of iron, gave no trouble, which was, no doubt, due to the shortness of the runs. Up to this time there was no very definite idea of costs, such as cost of electrode and power consumption. Another furnace was therefore built of the same type, and an effort made to run a ton of zinc concentrates in one run, keeping careful record of the power and electrode consumption, disregarding entirely the condensing of the zinc to spelter. This run was in two parts, one using metallic iron as a reducing agent, and the other using lime and coke according to the following reaction:

$$ZnS+CaO+C=Zn+CaS+CO.$$

The following results were obtained:

	Reducing Agent.	
	Iron.	Lime and Coke.
Kw. H. consumed	360	388
Pounds ore smelted	455	363
Lbs. reducing agent	193	Lime 164, Coke 33
Total lbs. charge	648	560
Kw. H. per lb. charge	0.556	0.692
Kw. H. per lb. zinc concentrate	0.79	1.07
Kw. H. per ton zinc concentrate	1580	2140
Per cent of zinc extracted (obtained by difference)	90	50

The above test, using iron as a reducing agent, was made in three separate runs, the furnace being allowed to cool down between runs. In using lime and coke the furnace was allowed to cool down four times. Copper-coated carbon electrodes 3 ins. (7.5 cm.) in diameter were used, and the carbon consumption per ton of zinc concentrate was 12 pounds (5.45 kg.). This furnace was lined with magnesite brick. The run did not show them to be superior to fire brick. Under these conditions the cover of the furnace suffered the most and had to be replaced twice.

The power consumption varied greatly, and it required constant moving of the electrode by the operator to keep the furnace running. The furnace was charged once an hour by the means of a hopper with a slide in the bottom. Immediately after charging, the zinc vapor issued from the ends of the condenser with great velocity, due to the small amount of moisture present. The charge was not preheated as it should have been. There was no separation of slag and matte. An analysis of the material tapped from the part of the run using lime and coke for reducing agent is as follows: Insoluble 8.6 per cent, FeO 13.2 per cent, S 24.3 per cent, Zn 24.3 per cent, CaO 25.1 per cent.

At this time it was decided that the most economical method of treating zinc concentrates could be attained by roasting them to oxide but leaving sufficient sulphur to form a matte as a collector for the precious metals. After some experimenting the practicability of the following reaction was proved:

$$Fe_2O_3+3C+2ZnS=2Zn+2FeS+3CO.$$

By this method the major part of the zinc is reduced from the zinc oxide by carbon, and the zinc in the sulphide form is reduced by iron which has been reduced by carbon from iron oxide.

THIRD FURNACE BUILT.

The next furnace constructed was to have a capacity of one ton of roasted zinc concentrates per day. The furnace was a radical departure from anything previously tried. The charge was fed into the fur-

nace through the upper electrode so as to introduce it directly into the arc. There were eight clay condensing tubes inclosed by heavy brick walls, with an arrangement to cool the tubes when they rose above the condensing temperature. (Fig. 3.).

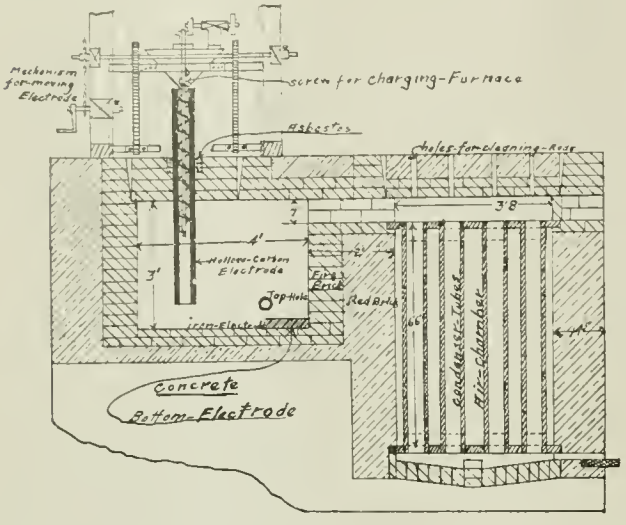


Fig. 3.

The condensing tubes being inclosed in heavy brick walls, it was thought that in time, about two or three days, the condensers would become overheated from the zinc vapors, and then it was proposed that the tubes be cooled to the right condensing temperature by air. This condensing temperature we were led to believe was between 450° and 515° C. Ingall's book on zinc smelting gives these figures. Later this condensing temperature was determined to be above 864° C. This is also consistent with theory, when it is considered that zinc boils under normal conditions at about 920° C.

CONDENSER DIFFICULTIES.

After several runs lasting from two to six days it was found impossible to heat the condensers to 450° C., let alone 864° C. The zinc was condensed in the form of blue powder, as was to be expected.

The brick work in this furnace was put in with all possible care, yet frequent explosions resulted from the leakage of CO gases into the air chamber surrounding the condensers. The openings were continually choking up with blue powder, and it was found rather hard to keep them clean. This character of condensing apparatus was too complicated to offer any success.

The means by which improvements in smelting were expected gave considerable trouble. The furnace was connected up without any regulating device to control the power, and as a consequence it was found impossible to keep the temperature constant. The charge was intended to be fed continuously through the hollow electrode by a screw, but, due to variance of fusing rate, the feed was continuously choking. The object of charging in this manner was to obtain lower power consumption per ton of charge. This was accomplished.

MECHANICAL DIFFICULTY.

The power consumed was from 1,100 to 1,300 kw. hours per ton of 50% zinc concentrate, but the mechanical difficulties still existed.

The hollow carbons gave considerable trouble by breaking. Later graphite tubes were used, which gave better results. The bottom electrode, which was of iron, as in the former furnaces, melted, and destroyed the bottom of the furnace with it. The furnace cover showed no deterioration whatever.

The furnace was then remodeled. (See Fig. 4.) In place of the iron electrode in the bottom a 6-in. (15 cm.) diameter graphite electrode was substituted. The smelting chamber was reduced in size, and a water rheostat was placed in series with the current as a means of controlling the power.

The condensing apparatus was replaced by three clay tubes 1 in. (2.5 cm.) thick, 4 ins. (10 cm.) inside diameter and 5 ft. (150 cm.) long. These were placed in a shallow brick chamber open at the top. These condensers were covered with varying thicknesses of dirt, as it was thought necessary to maintain the condensing temperature. With this device some spelter was obtained. From 4 to 5 in. of each tube was doing the condensing, and the greater part of each tube was too cold to condense. The condensing apparatus was next replaced by eight tubes 1 in. (2.5 cm.) thick and 4 ins. (10 cm.) inside diameter, all of different lengths, varying from 14 ins. (35 cm.) to 28 ins. (70 cm.). Two of these tubes were of carbon, the rest were of clay, and two of the clay tubes were partially filled with charcoal.

The ends of these condensers were luted with clay, leaving about 5/8 in. (1.5 cm.) diameter hole for the escape of CO gases and uncondensed zinc vapor. Pyrometers were constantly kept in the tubes. No

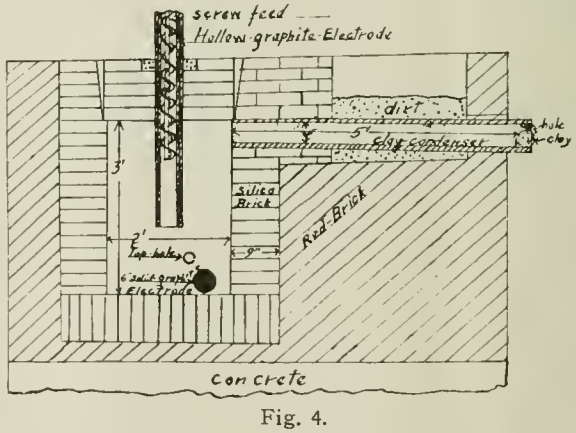


Fig. 4.

zinc could be condensed unless the inside surface of the condensers was above 840° C. and at 900° C. the condensers were too hot. The carbon tubes condensed no better than the clay tubes; the clay tubes containing charcoal did not condense quite as well as the tubes without charcoal.

At no time during this run was the zinc completely condensed, for there was always uncondensed zinc burning at the ends of tubes, and at all times the con-

densers would condense spelter if the temperature was around 864° C. From these results it was concluded that each of the tubes had a limited condensing capacity, and if the tubes were kept at 864° C., and the amount of zinc volatilized kept within the limits of the condensing capacity of tubes, there would be practically a complete condensation of the zinc.

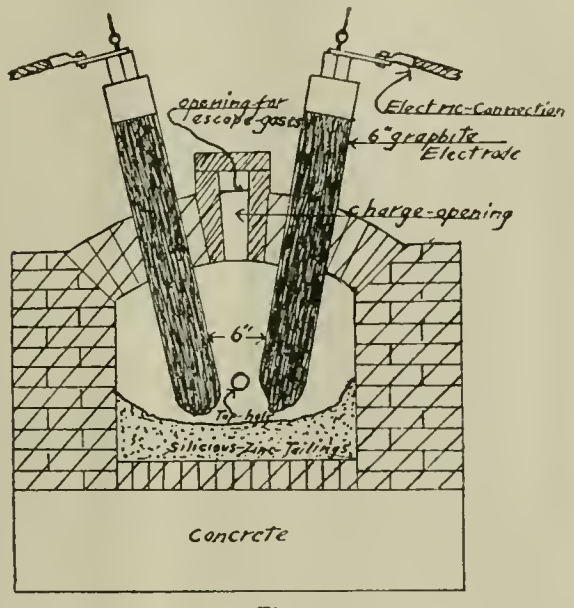


Fig. 5.

PRODUCTION OF SPELTER.

Another change was made in the furnace. Solid graphite electrodes 6 ins. (15 cm.) in diameter were used in place of the hollow ones, and the charge was introduced by means of a screw through one side and near the top of the smelting chamber. The furnace was run on barren charge until the condensers attained a temperature of 859° C.; then a charge containing zinc was introduced and fed at a rate so that very little zinc appeared in the flames burning at the end of the condensers. This was maintained for twelve hours, and the spelter condensed and recovered was 86.4 per cent of the amount charged into the furnace. Thus at last it was proved that spelter could be made with the electric furnace, but it was observed that the power consumption was approximately 4,000 kw. hours per ton of 50 per cent zinc concentrate.

The furnace bottom was giving trouble. It melted out almost as readily as the charge. This complicated matters, making the slag thick and pasty, and only occasionally did any matte appear with the slag, but the matte was always found when a furnace was torn down. The bottom electrode was consumed at about the same rate as the vertical one. This and other reasons made the furnace exceedingly hard to control. The destruction of the furnace bottom was attributed to the arrangement of the electrodes.

The condensation of zinc requires constant conditions, such as a quite uniform flow of gases and a constant temperature which can be easily varied. The next step was to improve the smelting part.

A small furnace was erected with two electrodes through the top. (See Fig. 5.) These were placed about 6 ins. (15 cm.) apart. The inside of the furnace was lined with silica brick, and the bottom covered 10 ins. (25 cm.) deep with silicious zinc tailings from mill jigs.

No efforts were made at the condensation of spelter, the zinc fumes passing into a flue and allowed to go to waste.

With this furnace numerous runs were made covering a period of thirty days. Slags of different composition were tried and the proportion of reducing carbon was determined. This work resulted in much useful information concerning furnace charges. We had no difficulty whatever in making slags and mattes and tapping them from the furnace, and the power and temperature could be kept constant or varied at will with practically no attention. Test runs on recovery of metals and power and electrode consumption were very satisfactory. The furnace was torn down, and showed practically no deterioration whatever; in fact, part of the tailings in the furnace bottom were not altered.

A larger furnace was constructed along these lines, fitted with eight conical condensers such as used by the zinc smelters in Kansas and Oklahoma.

A run was started, and for the first twenty-four hours was encouraging. Then the old trouble returned. The furnace would not respond to regulation, and no slag could be tapped. The apparent electrode consumption was enormous; 26 ft. (780 cm.) of 6-in. (15 cm.) diameter solid graphite electrodes were fed into the furnace in six days' time.

Something was radically wrong, and on opening the furnace it was found that a hole 6 ft. (180 cm.) below the bottom had been melted out. The electrode consumption had been very little; the electrodes when removed were 12 ft. (360 cm.) and 14 ft. (420 cm.) long, respectively. The trouble was caused by the arrangement of the electrodes. The operators in attempting to regulate the power had lowered the electrodes through the bottom of the furnace.

The hole in the bottom of the furnace was filled with silicious zinc tailings, and the electrodes placed at such an angle to each other (see Fig. 6) that when lowered they would meet at the bottom of the smelting chamber. The screw feed was abandoned, owing to the irregularity of air supply used in running it, and charging of the furnace was accomplished by means of a brick hopper with a graphite electrode for a slide in the bottom.

The furnace as now arranged was smelting for an actual running time of 30 days with five stops, during which time the furnace was allowed to get cold. During these runs the previous condensing experiences were repeated without any improvement. The

spelter that was condensed was found remarkably pure, assaying from 99.3 to 99.8 per cent zinc. The furnace gave no trouble in any way. Slag and matte were tapped every twelve hours.

For the time being the efforts at improving the condensers were abandoned and arrangements were made to recover all zinc products. To accomplish this a new furnace was built and special iron condensers

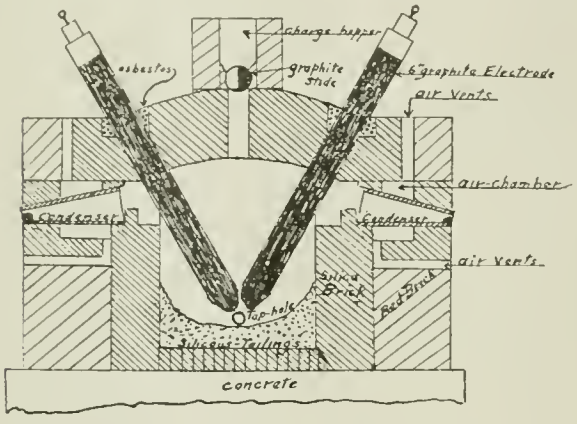


Fig. 6.

were made to recover the blue powder; also a bag house was used to catch the zinc oxide in fumes. Fig. 7 is a view of the blue powder condenser. A 12-day run was made without difficulties of any kind. The charge was fed in every hour, and slag and matte tapped every 12 hours.

The metallurgical results will follow.

This furnace in its present improved form is about all that can be expected of any furnace. There are far less difficulties encountered than in running an ordinary blast furnace. The deterioration of the furnace is small. Such a furnace should run from six months to a year without any extensive repairs. Large units can be constructed by merely the addition of more electrodes, and there is no reason why units of 25 to 50 tons each could not be operated as easily and cheaply as the one-ton units.

In connection with the condensing experiments a small resistor type of furnace was constructed. (See Fig. 8) This furnace was made with a view to duplicating the conditions existing in the present-day zinc retort, with the exception that electrical heat was used instead of gas or coal. The essential parts of the furnace were a rectangular brick chamber having a resistor of graphite blocks in the bottom, connected to an electrode at each end. The arrangement of this furnace was such that the heat was always under control. There was one condenser of the same type as used in retort smelting. The furnace was charged intermittently with roasted zinc concentrators and coke and coal.

In operating this furnace great care was taken in regulation of the heat so as to have the same conditions as in the retorts. It was noticed that the zinc began to volatilize before the condensers were hot enough to condense it to spelter, and that after the condensers had reached the right temperature there was more zinc volatilized than it would condense; and when the heat was reduced to cut down the volume of zinc vapor, the condenser would get too cold. This condenser when at the right temperature, which could be easily maintained, would condense two pounds of spelter per hour with approximately the same amount of zinc vapor passing through without condensing. There could be no doubt whatever as to the gases being of the same composition as in the retort.

These experiments were repeated a number of times, and the results were always the same, and to me they prove conclusively that the failure to condense zinc to spelter in the electric furnace is due to the difficulties in maintaining sufficient condensing area at the right temperature near the source of volatilization.

METALLURGY.

In the operation of the electric zinc furnace the composition and condition of the smelting charge is quite as important as the furnace. More care must be exercised in making up furnace charges than in ordinary blast furnace practice. The charge must be such that at all times there is a perfect reducing atmosphere in the furnace; the slag must be such that deterioration of the furnace lining is reduced to a minimum, and with a sufficiently high formation temperature to volatilize the zinc. A matte must be made that is uniform in composition and is readily tapped

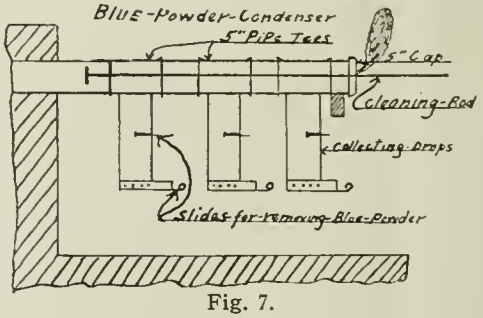


Fig. 7.

from the furnace, and made in sufficient quantity to effect a good saving of copper, gold and silver. The proportion and nature of the reducing carbon is important. As before mentioned, a perfect reducing atmosphere must be maintained, and at the same time the reducing carbon must be completely consumed. If an excess is added, it can not be burned by an air blast as in blast furnace practice, and the only oxygen available for its consumption is that held in combination by the constituents of the furnace charge.

The physical character of the charge is quite as important as the chemical for the best work. The charge constituents should be finely divided so as to allow the various reacting elements to be in intimate contact with one another, thus insuring more perfect and economical results. But the charge must not be too fine when charging in loose rather than in brick-

ette form. The particles should be of such weight or size as to readily settle from the zinc vapors and gases passing outward into the condensers. If the particles are too fine they are apt to find their way into the condensers in the unmelted condition.

It is necessary to have the charge absolutely dry. The presence of water even in small quantities is serious, due to the oxidizing of the zinc vapor by

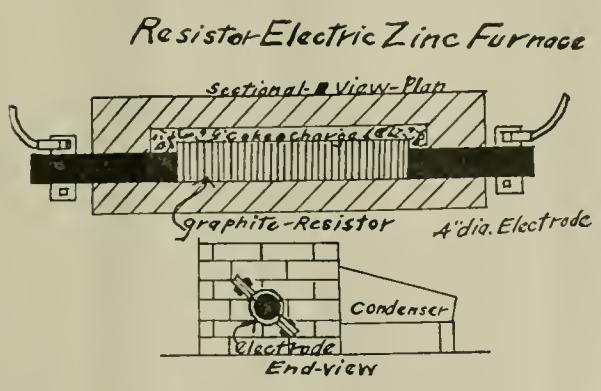


Fig. 8.

decomposition of the water. What is still more serious is the instantaneous generation of steam and other gases, causing a great increase in the velocity of gases, thus disturbing the condensation of the zinc in the condensers and thereby causing a loss of zinc and also a loss of silver and other metals, due to furnace charge being blown outward into the condensers.

For reasons above outlined, if it is not possible to mix the charge with hot calcines from the roasting furnace and then immediately feed it to the electric furnace, there must be a preheating furnace to heat the charge before introducing it into the electric zinc furnace.

SLAGS.

The making of slags is governed by the nature of the furnace linings, and these are dependent on the nature of zinc concentrate or ore to be smelted. If the concentrates are high in iron and low in silica, then a basic slag high in iron is made, and consequently a basic furnace lining (such as magnesite brick) is used; and if the reverse is the case, then high-silica slags with silicious furnace linings are used.

The principle used in the elimination of zinc from slags was to make slags of such high formation temperature as to practically volatilize most of the zinc before slagging of the charge begins.

In silicious slags the high percentage of silica is the principal controlling factor. In basic slags the percentage of reducing carbon is increased, which for practical purposes gives the same effect.

In the work I have been identified with we have had practically no difficulty in eliminating zinc from either basic or silicious slags. The degree of elimination depended on the quantity of power used. Following are analyses of slags showing how zinc elimination can be varied:

	Zinc	Copper	Iron	Insoluble	Silver	Gold
Slag No. 1....	0.3%	0.24%	16.1%	66.2%	1.2 oz.	trace
Slag No. 2....	1.6	0.13	19.2	57.5	0.6	trace
Slag No. 3....	5.5	0.47	22.9	45.5	4.1	0.01 oz.
Slag No. 4....	8.5	0.38	23.5	44.4	2.1	trace

MATTE.

In the treatment of complex ores the other metals, gold, silver and copper, are also recovered. This is accomplished by producing a collector (matte) similar to the lead button in crucible fire assaying.

In the earlier work it was attempted to use as a collector a matte consisting principally of iron sulphide, but its use was not attended by any degree of success. The matte formed was very irregular in composition, varying from metallic iron to iron sulphide. The amount of matte formed was also irregular, and it was found necessary to add copper ores until the furnace charge would assay in the neighborhood of 1 per cent copper in order to get a matte uniform in quantity and composition. The quantity of matte was varied by varying the percentage of sulphur in roasted zinc calcines. Zinc calcines were successfully treated that varied from 2 to 15 per cent sulphur. The best results were obtained between 5 and 7 per cent sulphur. One of the important reactions in this connection is:

$$Fe_2O_3 + 3C + 2ZnS = 2FeS + 2Zn + 3CO$$

or $Fe_2O_3 + 3C = 2Fe + 3CO$ and $2Fe + 2ZnS = 2Zn + 2FeS$.

REDUCING CARBON.

Coke was found to give the best results. When coals were used it was noticed that the condensing of the zinc was seriously interfered with, due to deposition of fine carbon or soot in the condensers from the decomposition of the hydrocarbons in the coal.

As a basis of determining the amount of reducing material, there was computed from analysis the percentage of oxygen present in a unit charge, and coke was added in sufficient quantities to form CO with the total oxygen. Usually a trial run was necessary to determine the right proportion. The evils of an excess of coke are the formation of infusible compounds and the consequent difficulties in tapping the furnace.

The immediate remedy is to add charge without carbon until the excess of coke is consumed. This is readily determined by the physical character of the slag.

RECOVERY OF LEAD.

The lead in the ores experimented on was low, varying around 1 and 2 per cent, and in all cases it was almost completely volatilized with the zinc. But I do not see any reason why zinc-lead concentrates could not be successfully treated. It would require a varying of the heat so as to reduce lead first, which, if necessary, could be tapped from the furnace, and

then continue for the volatilization of the zinc—all of which is well within the limits of the electric zinc furnace.

TREATMENT OF BLUE POWDER.

At the present time the only drawback to electric zinc smelting is the inability to condense completely the zinc volatilized to spelter. Of course, this refers to operations conducted on a commercial basis, and not to small test runs where care and attention can be exercised, which is impossible on a commercial scale.

The zinc vapor as now condensed in the electric zinc furnace is mostly metallic zinc, but the greater part is so finely divided that it is impossible to melt into bars. This is called blue powder or zinc dust, the name blue powder being derived from its physical appearance. Blue powder, as a rule, has the same chemical analysis as spelter; the difference between them is purely physical. Attempts to melt blue powder in open vessels have up to this time proven failures, due to the oxidation of the minute particles of zinc to zinc oxide before consolidation of the particles could take place.

Blue powder can be melted into spelter by the use of pressure and heat. In the experiments performed by the author (which were not original) this was accomplished by placing the blue powder in a cylinder having notches at one end. This cylinder was placed on a solid block in an upright position, with the notched end down so as to allow for the escape of the molten zinc. Into the other end of the cylinder was placed a loosely-fitting plunger connected to a screw so that pressure could be applied. Into this cylinder blue powder was placed and put under pressure by means of screw and plunger. The cylinder was then heated up to temperature from 600° to 700° C. By this means from 80 to 85 per cent of the zinc could be squeezed from the blue powder.

Another method was tried—a hot electrolytic process devised by Warren F. Bleeker and described by him in the Transactions of the American Electrochemical Society, 21, 359 (1912). In this process a molten bath of zinc chloride is made use of. The zinc chloride is placed in a vessel which is a good electrical conductor, such as iron or graphite. This pot is connected electrically as the cathode of a direct current circuit, and into it is placed a graphite or carbon electrode which is connected as the anode in the same circuit. The bath is then maintained at a temperature above that of molten zinc, and direct current passed through it. The blue powder to be melted is stirred into the bath, where it very quickly melts into spelter and settles to the bottom of the spot, whence it can be removed by tapping.

Experimenting with this process was not extensive enough to warrant giving any figures. It might be noted, however, that, with the bath in good fluid condition, and with all electrical connections clean, as much as 10 pounds (4.5 kg.) of spelter was melted from blue powder with an expenditure of only one kilowatt hour of power.

The experiments were conducted in an iron pot, and, further, the blue powder used in tests was condensed in iron condensers. This made the resulting spelter high in iron (from 1 to 2 per cent). Efforts were made to refine this spelter by the ordinary fire methods, that is, by keeping the impure zinc in a quiet state of fusion near its melting point, by which means the impurities, iron and lead, would settle to the bottom, the lead almost in the pure form, and the iron as zinc-iron alloy analyzing as follows: Zinc 91.3 per cent; iron 5 per cent, and lead 1.5 per cent. This method of refining gave, roughly, 50 per cent of the spelter suitable for market, and over 90 per cent of the lead could be recovered, but the zinc-iron alloy, representing about 50 per cent of the zinc recovered from blue powder, could only be placed on the market by selling to retort smelters, where it would be redistilled.

Some experiments were conducted with a view of devising a process of refining this zinc-iron alloy without distillation. Iron and sulphur unite readily at the melting point of the zinc-iron alloy to form iron sulphide. A scheme of removing the iron from this alloy by means of sulphur looked very promising, but, as sulphur vaporizes at a temperature below that of melting zinc, some other means had to be used in introducing the sulphur. Iron pyrite (FeS_2) breaks down at 565° C., giving up half of its sulphur.

Several lots of zinc-iron alloy were melted, and into them was stirred finely ground pyrite (FeS_2), while one experiment was tried with galena (PbS). The results showed that in every case the iron content was reduced (the liberated sulphur uniting with iron forming FeS, which is infusible at temperature of test), and, while the experiments were not complete, the results were encouraging and indicate that this class of impure spelter may be refined by other and cheaper means than by distillation.

DESIGN OF A MORE EFFICIENT CONDENSER.

It has been demonstrated that zinc vapor can be condensed to spelter with a fairly good efficiency with the electric zinc furnace for short periods where great care is taken to maintain the right temperatures. In the present retort method of distilling zinc it has been shown that about 7 per cent of the heat in the coal is actually utilized for the work of vaporizing the zinc, and 93 per cent is lost by radiation, etc. A great part of this so-called lost heat is used in heating the enormous mass of brick in the furnace, and this in turn tends to keep a certain constant temperature around the furnaces and condensers, and without this heat (or, rather, if 93 per cent of the heat was utilized for the vaporization of the zinc, and only 7 per cent lost by radiation, etc., which is nearly the case with the electric zinc furnaces), I am satisfied that the retorts would not produce a greater percentage of spelter than the electric zinc furnace.

Electric zinc furnaces constructed on the same principles of heating as retort zinc furnaces have given as good condensing results. In these furnaces the heating of the furnace charge is accomplished by the radiation of heat from an electric arc located above the charge. Practice has proven this a very inefficient means of electric heat, yet so far as condensing is concerned it gives the best results.

APPLICATION OF THE ELECTRIC ZINC FURNACE.

The following, worked out on a one-ton unit, will give a fair idea of the costs:

Costs Per Ton of Pay Charge.

Roasting	$ 1.00
Supt. and Assay Office, etc.	1.00
Labor based on 33 ton plant	.83
Power—1401 Kw. hours, @ 0.332 cent	4.65
Depreciation of plant	.40
9.5 lbs. electrodes, @ 14 cents	1.33
0.1215 tons coke screenings, @ $5.00 per ton	.60
440 lbs. matte. Cost of marketing	2.86
Total cost	$12.67

With the electric zinc furnace the following extractions can be depended upon for the above costs: Zinc extraction, 85 per cent; copper extraction with 5 per cent copper in charge is over 95 per cent, and with 1.5 per cent copper in charge is 84 per cent; silver extraction, 65 to 72 per cent; gold extraction, from 98 to 100 per cent.

The gold, silver and copper are recovered in the form of a copper matte. The difference in the value of the metals and that actually obtained from them is called the cost of marketing the matte.

The zinc as obtained with the process at its present perfection of condensation with the above costs contains only 30 per cent spelter ready for the market. The remaining 70 per cent of the zinc is obtained in the form of an 80 per cent zinc product, as blue powder and some zinc oxide. This zinc as produced by the electric zinc furnace would be worth $4.36 a hundred pounds when spelter is selling at $5.50 per hundred, that is, when the 30 per cent spelter producer is placed on the market and the remaining 70 per cent of the zinc in the form of an 80 per cent product is shipped to zinc smelters on an ore basis treatment charge. Greater economies could be effected if the electric smelter had retorts of its own to treat this high-grade concentrate of blue powder and zinc oxide.

If a straight zinc concentrate assaying 50 per cent zinc is shipped to a zinc smelter, the probable basis of settlement would be as follows: 85 per cent of the zinc content at market price of spelter, with $16.00 deducted for treatment charge. With spelter at 5.5 cents per pound, one ton of 50 per cent concentrate is worth $30.75.

The electric smelter, after deducting $12.67 for treatment, would return for the same concentrate $23.41. But if a complex zinc concentrate containing approximately 10 per cent iron with copper, gold and silver values were to be considered, the difference would be greatly in favor of electric smelting. The penalties on iron, etc., and the poor extraction of copper, gold and silver by the retort smelters would make it impossible for them to compete with the electric zinc smelter.

In the West complex zinc ores are abundant, and in some cases water power can be obtained near the mines, which would be an added advantage to the electric smelter by effecting a saving to the miner on freight on concentrates.

Another probable source of increased revenue would be the sale of zinc products, as zinc oxide, for the paint industry. Statistics show that, in 1910, 16 per cent of all zinc produced in the United States was sold as zinc oxide, and in this form brought 0.1 of a cent more per pound than if sold as spelter. There is absolutely no difficulty in making zinc oxide suitable for paint by the electric furnace. The principal accessory required is a big house and packing plant. A small percentage of the product could be sold as blue powder at prices about equal to that of spelter.

The Rocky Mountain States of the West present great opportunities for the treatment of complex zinc ores by the electric furnace. As the process stands today it should be a big success on complex zinc ores.

The electric zinc furnace is young, and in the course of operations many improvements will be made and costs greatly reduced.

The production of coke in Illinois in 1912 amounted to 1,764,944 short tons, valued at $8,069,903, against 1,610,212 tons, valued at $6,390,251, in 1911, according to E. W. Parker, of the United States Geological Survey. The average value per ton advanced from $3.97 to $4.57. In spite of the increase in production Illinois dropped from fourth to fifth place in rank among the states because of the much larger increase in Indiana that followed the putting in blast of the entire plant of 560 Koppers ovens of the United States Steel Corporation at Gary, which advanced that state from sixth to third place.

All the coke produced in Illinois in 1911 and 1912 was made in retort ovens, much of the coal being drawn from West Virginia mines; no beehive coke was produced in the state. In some of the ovens the charge consists of a mixture of West Virginia and Illinois coals in the proportions of 4 to 1. This has been found to make an entirely satisfactory coke. There were four retort plants, with a total of 568 ovens in operation in 1912. One of these plants consisted of 240 Semet-Solvay ovens, operated by the By-products Coke Corporation at South Chicago. The plant has been enlarged three times, the latest addition of forty ovens being completed in 1912.

Thirteen of the same kind of ovens were operated by the North Shore Gas Co., at Waukegan, having been completed in 1912. These ovens are heated by producer gas made from the coke. All the retort gas goes to the city mains.

PROGRESS OF WOOD PULP SILK MAKING.*

Within a year and a half two new inventions have been brought out in France for the manufacture of artificial silk, one at Rouen and the other at Harfleur, a suburb of Havre. The latter, however, which is being exploited by a prominent French cotton firm, is in the experimental stage. Both of these inventions are based on the use of raw cotton instead of woodpulp, and both claim to have overcome the difficulty found with the viscose patent, that of non-washing. The company having its works near Rouen is at present turning out daily about 580 pounds of artificial silk, some of which is entrusted to a Lyon silk manufacturer who is assisting the firm in its enterprise, the balance being sent to a well known firm of American silk manufacturers, who are said to be most enthusiastic about it.

It is said that skeins of silk produced by this firm have been submitted to an independent London expert, by whom they were soaked in water for some time, wrung out, and then rough dried in an ordinary oven at a high temperature. On comparison with unwashed samples the expert declared that he could not find any difference as to either brilliance of color or tensile strength. The inventors claim that a test dress made wholly from this silk, without any admixture of cotton, wool, or real silk (such as is necessary with woodpulp silk), was worn during the summer of 1911, and that on examination after the text experts declared that it had worn quite as well as, if not better than, true silk.

From a statement in the Manchester *Guardian* it appears that for some years past the Vereinigte Kunstseide Fabriken, Frankfort on the Main, one of the largest Continental producers of artificial silk by the guncotton process, has suffered seriously from the keen competition of the newer makers by the cuprammonium and viscose systems, and the handsome profits earned during the early years of the undertaking have given way to heavy losses, last year's balance sheet disclosing a deficit of nearly $200,000. Some time ago the directors decided to take up the viscose method, and began to manufacture by it, a procedure which resulted in a suit being brought against them by the Verenigte Glanzstoff-Fabriken, Elberfeld, who claimed that the Frankfort firm were infringing their patents. Judgment was given against the defendants, who gave notice of appeal. In the meantime they worked out a modification of the original process which they assert was in no way an infringement of the Elberfeld one. The product marketed appeared to be quite satisfactory, but the cost of manufacture is understood to have been much greater. It is now officially announced that an understanding has been arrived at between the two firms. To clear off the heavy loss of the past few years, the capital of the Frankfort company is being reduced from $868,000 to $348,000, and new shares to the amount of $366,000 issued, thus bringing the capital up to $714,000. A large proportion of the new shares will be taken up by the Elberfeld concern, who will also be represented on the board by two directors. They also agree to grant a license to the Frankfort company, allowing them to manufacture according to their viscose patents and also to give them the full benefit of their experience in working the process.

A number of lawsuits brought against competitors for the infringement of patent rights have been satisfactorily settled. The English subsidiary company formed a few years ago to work the cuprammonium process of the Elberfeld concern has not yet been in a position to pay a dividend, and it was stated that it had been decided to give up the cuprammonium process at the English works and begin producing by the viscose method. The French subsidiary company has paid a dividend of 22½ per cent and the Austrian a dividend of 10 per cent. Two years ago the capital was increased from $500,000 to $1,190,000, shareholders receiving free one new share for each share held. It was said that this was decided upon in order to prevent the rate of dividend paid from appearing unduly large, and it was mentioned at this year's meeting that a capital increase on similar lines would again be made.

* From paper.

The zinc output of Colorado (in terms of spelter and zinc in zinc oxide) was 132,222,812 lbs. in 1912, as compared with 94,607,456 lbs. in 1911, an increase for 1912 of 37,615,356 lbs. in quantity and of $3,730,749 in value. Lake County, with an increase for the year of 34,335,337 lbs., furnished 105,945,783 lbs., or 80 per cent of the state yield. The output of zinc carbonate ore from Leadville was 142,782 tons of 29.2 per cent zinc, against 83,905 tons of 31 per cent zinc in 1911. The zinc sulphide ore shipped increased from 79,376 tons of 23.3 per cent zinc in 1911, to 104,148 tons of 23.8 per cent zinc in 1912. Increased production of zinc was also made in Chaffee, Clear Creek, Dolores, Eagle, Fremont, Ouray, Pitkin, Saguache, San Juan, and Summit counties, and appreciable decreases were made in Mineral, Park, and San Miguel counties. Zinc production in concentrates amounted to 46,053,954 lbs., and in crude ore to 86,168,858 lbs. The number of deep mines producing metals in 1912 was 856, against 861 in 1911. The average total recovered value per ton of ore produced increased from $13.50 in 1911 to $14.32 in 1912. In 1912 2,576,626 short tons of crude ore mined in Colorado were sold or treated, an increase of 198,690 tons over the output of 1911. Of this total, 1,435,837 short tons went to gold and silver mills, 523,063 tons went to mills for cencentration only, and 617,726 tons went crude to smelters; 224,722 tons of concentrates also went to smelters.

METALLURGY.

CUPOLA STUDIES.

By H. B. PULSIFER.

In 1908, Professor H. McCormack, inaugurated foundry control runs for the students taking the course in "Metallurgy of Iron and Steel" at the Armour Institute of Technology.

Reports of two of these runs were published in "Metallurgical and Chemical Engineering," the first, 1908, VI, p. 21, the second, 1909, VII, p. 391. A recent number of "The Foundry"* contained a much patched-up and doctored account of one of these earlier runs, the paper did not even acknowledge Professor McCormack's entire responsibility for all the original work.

Since the runs have proven of great value to the students they have been continued each year with increasing effort to get at the truth and attain completeness. Professor McCormack supervised several runs; Instructor McMullen then had charge for a time until the author was given the metallurgical work in the fall of 1911.

Various circumstances render the control work incomplete or poorly made; the foundry work is in the mechanical department and the students in chemical engineering merely assemble with the required apparatus on the afternoon of the run and do their best to make the necessary observations and get the proper samples. The mechanical department offers every courtesy and the foundry is put to considerable inconvenience in preparing for and accommodating the extra squad of students. This is most cheerfully accepted and the help of Instructor Larsen and his assistant Mr. Davis aids much in the success attained. In spite of considerable personal effort of all concerned the task is so great and so much is demanded of the apparatus, observational and analytical skill, and particularly accuracy in sampling, that exact results are hard to attain and great improvement is yet ahead.

The actual work is entirely carried out by the students. They do the sampling, setting up of instruments and observe and record the data. They also do all the subsequent analyses and finally each fits in his own work with that of the others to make the finished report. 19 students, under 5 excellent squad leaders, had part in the run of April 4th, 1913; each handed in a report substantially as indicated on the following sheets. It is considered a part of the work to consult the previous reports and correct and improve; some also devised their own methods of reaching the desired results with consequent variations in figures. We consider it very creditable that students should accomplish even as good work as here recorded; failure of any one set of observations affects the whole work and that no complete failure resulted was very gratifying. Doubtless more concordant figures would result from repeating the experiment; this is not possible in the time allotted to accomplish this and the other work required during the semester.

The student reports have the sheets numbered and allotted according to the following scheme:

FOUNDRY RUN OF APRIL 4, 1913.

SHEET I. CHARGE SHEET.

Charge.	Material.	Time.	Lbs. Iron.	Lbs. Coke.
1	Coke	1:00-1:18	...	300
2	½ Scrap, ½ Pig	2:03-2:09	900	60
3	⅞ Scrap, ⅛ Pig	2:17-2:19 2:30-2:31	500	60
4	½ Scrap, ½ Pig	2:36-2:38	500	60
5	⅓ Scrap, ⅔ Pig	2:51-2:53	550	60
6	⅔ Scrap, ⅓ Pig	3:05-3:06	550	60
7	½ Scrap, ½ Pig	3:10	400	..

Furnace Lighted	12:58
Wind On	2:11
First Iron tap hole closed	2:15
Small Ladle, test sample	2:27
Large Ladle, half full	2:36
Blast off by mistake	2:48-2:49
1,200 lbs. out, sample	2:50
1,700 lbs. out, sample	2:57
Sample	3:06
Blast Off	3:23

	Pounds.
Total Iron Charged	3,400
Total Coke Charged	600
Scrap Iron Charged	1,700
Pig Iron Charged	1,700
Coke in Drop	136
Slag in Drop	197
Melted Iron in Drop	103
Unmelted Pig Iron in Drop	77
Weight of All Iron Recovered	3,184
Net Amount of Iron Melted	3,323

SHEET II. BLAST DATA.

Differential Gauge in Blast Pipe	.77 in. Aq.
Differential Gauge in Stack	.10 in. Aq.
Manometer in Cupola Jacket	8.62 in. Aq.
Average Diameter inside Blast Pipe	6.75 inches
Average Diameter inside Stack	19. inches
Loss of Air (leaks) between Gauge and Stack	5%
Average Temperature of Blast Air	25° C.
Average Temperature of Stack Gases	920° C.
Length of Run	71 minutes
Cross-section of Blast Pipe	.248 sq. ft.
Cross-section of Stack	1.97 sq. ft.
Barometer	735. mm.
Barometer + 8.62 in. Aq.	751. mm.
Weight of 1 cu. ft. dry air at 760 mm. and 0° C.	.0807 pound
Weight of 1 cu. ft. Water	62.4 pound
Weight of 1 cu. in. Water	.036 pound
Weight of 1 sq. in. Air, 1 ft. deep	.00056 pound
Weight of 1 Liter Dry Air, 45° Lat., 760 mm. 0° C.	1.2934 gm.
Weight of 1 Liter Dry Air, 45° Lat., 760 mm., 0° C.	.00285 lb.
1 Cubic Foot	28,314 cu. cm.
1 Kilogram	2.2046 pound.

Blast Gauges read every two minutes.

Stack Readings and Samples taken with Closed Door as nearly as possible on four minute intervals.

SHEET III. GAS ANALYSIS. (STACK.)

Time.	CO_2.	O_2.	CO.	Remainder.
5	16.8	0.0	2.2	81.0
9	15.0	0.0	5.8	79.2
20	15.5	0.0	5.0	79.5
29	14.6	0.0	6.6	78.8
35	14.8	0.0	4.8	80.4
43	13.0	0.0	8.0	79.0
48	13.4	0.4	6.2	80.0
54	11.7	0.4	6.9	81.0
59	11.0	0.6	7.4	81.0
63	11.4	0.2	9.2	79.4
67	9.4	0.0	11.0	79.6
71	9.6	0.2	8.8	81.4
Weighted Average..	13.50	0.12	6.38	80.0
Av. before Blast On.	7.6	8.6	2.3	81.5
Sample from Charge.				
Average during Run.	9.1	1.4	12.4	77.1

Temperature of Iron.

1,000° Thwing.
900° Pyrometer.
960°
1,300°
1,250°
1,200°
1,250° Average Temperature (Observed), 1,131° C.
1,100°
1,050° Corrected Temperature: 1,131×1.29=1,460° C.
1,200°

SHEET IV. ANALYSES.

	T. C.	G. C.	Si.	Mn.	P.	S.
Pig Iron	3.42	2.98	3.36	.62	.61	.018
Scrap Iron	2.88	2.18	2.03	.39	.55	.018
Castings	3.34	2.59	2.49	.41	.62	.070

Coke—	Calories.	Moist.	V. C.	M. Ash.	F. C.	S.	P.
Regular	6,430	.4	1.58	9.58	88.44	1.13	.012
In Drop	5,900	.08	0.000	9.56	90.33	1.13	.012

Limestone—None Used.

Slag—	%
Coarse Metallic Iron	28.0
Fine Metallic Iron (Iodine)	8.0
Silica	34.69
Iron as Ferric Oxide	23.52
Alumina	.50
Magnesia	4.72
Lime	None
Phosphorus	.21
Sulphur	.39

Coke Ash—	
Silica	38.55
Ferric Oxide and Alumina	36.83
Lime	5.00
Magnesia	1.04

SHEET V. AIR RECEIVED IN CUPOLA.

$$.0807\times\frac{275}{298}\times\frac{751}{760}=.07358=\text{Wt. 1 cu. ft. of Pipe Air.}$$

$$\frac{.77}{12}\times\frac{62.4}{.07358}=54.42=\text{Head of Air in Feet.}$$

$$\sqrt{2\times32.2\times54.42}=59.21=\text{Velocity of Pipe Air.}$$

$$59.21\times60.71\times\frac{275}{298}\times\frac{751}{760}\times.248=57{,}060\text{ cu. ft. Air Passing Gauge.}$$

57,060—2,853=54,209=Air Entering Cupola. (5% Loss.)

SHEET VI. GAS EVOLVED.

	pounds.
1 cu. ft. CO_2 weighs (760 mm., 0° C.)	.1166
1 cu. ft. CO weighs	.0738
1 cu. ft. O_2 weighs	.0843
1 cu. ft. N_2 weighs	.0738

$.1350\times.1166=.0157$
$.0012\times.0843=.0001$
$.0638\times.0738=.0047$
$.8000\times.0738=.0590$

$.0795$

$$.0795\times\frac{275}{1195}\times\frac{735}{760}=.0177=\text{Wt. of 1 cu. ft. Gas in Stack.}$$

$$\frac{.10}{12}\times\frac{62.4}{.0177}=30.6=\text{Head of Gas in Feet.}$$

*The Foundry, Vol. 10, 10: p. 408.

$$\sqrt{2\times32.2\times30.6}=44.4=\text{Velocity of Gas in Stack.}$$

$$44.4\times60\times71\times1.97\times\frac{275}{1195}\times\frac{735}{760}=82{,}850.$$

82,850=Volume of Gas Escaping through Stack, Reduced to Standard Conditions.

SHEET VII. HEAT LOST BY RADIATION.

Average Temperature of Lower Room Air..... 20.9° C.
Average Temperature of Lower Furnace Section.... 37.0° C.
Average Temperature of Middle Furnace Section... 47.0° C.
Average Temperature of Upper Furnace Section.... 32.0° C.
Average Temperature of Upper Room Air..... 31.5° C.
Areas—
Lower ..... 11′-4″ circ. × 3′-4″ high = 38 sq. ft.
Middle ..... 7′-4″ circ. × 2′-4″ high = 17 sq. ft.
Upper ..... 7′-4″ circ. × 8′-6″ high = 62 sq. ft.

$H=K(T_1^4-T_2^4)$.
$K=7.66\times10^{-11}$ gram calories per sq. cm. per min.
T_1=Absolute Temperature of Surface.
T_2=Absolute Temperature of Surroundings.
Lower Surface: 35,200 sq. cm.
$T_1=37+273=310°$
$T_2=21+273=294°$
Middle Surface: 15,750 sq. cm.
$T_1=47+273=320°$
$T_2=21+273=294°$
Upper Surface: 57,500 sq. cm.
$T_1=32+273=305°$
$T_2=31+273=304°$

$$H=7.66\times10^{-11}\times\left[\begin{array}{l}57{,}500\ (305^4-304^4)+\\15{,}750\ (320^4-294^4)+\\35{,}200\ (310^4-294^4)\end{array}\right]\times74$$

$=765.8\times74$
$=56669.2$ calories
$=56.7$ Calories.

SHEET VIII. HEAT ABSORBED BY CUPOLA.

Inner Diameter	.56 m.
Height of Lining	4.7 .m.
Thickness of Lining	11 m.
Specific Heat of Brick	2.26
Specific Gravity of Brick	2.2

$$\text{Average Temperature of Lining, } \frac{1{,}000-35}{2}=483°\text{ C.}$$

$.235\times4.7\times1{,}000\times2.2\times.26\times483=205{,}256$ Cal.

Heat in Unconsumed Coke—
136 lbs. = 62.0 Kg.
Specific Heat = .22.
Temperature = 1460° C.
$62\times.22\times1460=19{,}850$ Cal.

Heat in Slag—
197 lbs. = 89.5 Kg.
$89.5\times550=49{,}225$ Cal.
(Assumes total Heat at 550 Cal. per Kg.)

SHEET IX. HEAT ABSORBED BY IRON.

Unmelted Pig Iron = 77 lbs.

$$\frac{77}{2.2}\times.113\times1{,}200=4{,}800\text{ Cal.}$$

Melted Iron = 3,323 lbs.

$$\frac{3323}{2.2}\times1{,}205\times.113=205{,}570\text{ Cal.}$$

$$\frac{3323}{2.2}\times69=104{,}200$$

$$\frac{3323}{2.2}\times.22\times230=76{,}360$$

386,130

Sensible Heat in Evolved Gases—

$$CO_2\ \frac{405.3}{2.2}\times\frac{3.69}{6.42}\times\frac{11}{3}\times895\times.288=100{,}100$$

$$CO\ \frac{405.3}{2.2}\times\frac{2.73}{6.42}\times\frac{7}{3}\times895\times.260=42{,}550$$

$$N_2\ \frac{405.3}{2.2}\times\frac{3.69}{6.42}\times\frac{11}{3}=388.4=\text{Kg. } CO_2.$$

$$\frac{80.00}{13.50}=5.92.$$

$$388.4\times\frac{1.26}{1.98}\times5.92\times895\times.260= \quad .340,500$$

483,150

SHEET X. HEAT IN FUEL.

1. Potential; Calories by Bomb—

$$\frac{600}{2.2}\times6,430=\text{Gross Calories} \quad 1,753,460$$

$$\frac{136}{2.2}\times5,900=\text{Calories in Drop} \quad 364,620$$

Net Available 1,388,840

Potential; Calories from Net Carbon.

405.3×8,130=1,498,000 Net Available.

2. Actually Developed; from Net Carbon.

405.3 lbs. Carbon consumed to Gas containing 13.50% CO_2 and 6.38% CO.

$$405.3\times\frac{3.69}{6.42}=233.0 \text{ lbs. Carbon to } CO_2.$$

$$405.3\times\frac{2.73}{6.42}=172.3 \text{ lbs. Carbon to CO.}$$

	Calories.
$\frac{233.0}{2.2}\times8,130=$	860,967
$\frac{172.3}{2.2}\times2,450=$	191,835
Calories actually developed	1,052,800

Actually Developed; from Blast and Stack Data.

Blast—

$$54,209\times\left[\left(\frac{13.5}{100}\times\frac{.1166}{2.2}\times8.130\times\frac{3}{11}\right)+\left(\frac{6.4}{100}\times\frac{.074}{2.2}\times2,450\times\frac{3}{7}\right)\right]=$$

1,029,970 Calories.

Stack—

$$82,850\times\left[\left(\frac{13.5}{100}\times\frac{.1166}{2.2}\times8.130\times\frac{3}{11}\right)+\left(\frac{6.4}{100}\times\frac{.074}{2.2}\times2,450\times\frac{3}{7}\right)\right]=$$

1,501,300 Calories.

SHEET XI. HEAT FROM SLAG FORMATION.

Silicon from Iron to SiO_2—

$$\frac{3.36+2.03}{2}=$$

2.69 = % Si in Charge Iron.
2.49 = % Si in Castings.
.20 = % Si Oxidized.

	Calories.
$\frac{3323}{2.2}\times.002\times7,400=$	22,200
Iron Burning to FeO— $\frac{197}{2.2}\times\frac{23.50}{100}\times\frac{112}{160}\times1,173=$	18,110
FeO to FeO.SiO_2— $\frac{197}{2.2}\times\frac{143.6}{159.5}\times\frac{23.52}{100}\times147=$	2,786
	43,096

(Allow other developed heat to be balanced by the neglected quantities.)

SHEET XII. CARBON BALANCE.

Carbon Charged—	Pounds.
Carbon in Coke, 600×.89=	534.0
Carbon in Drop, 136×.90=	122.4
	411.6
Carbon Gained by Iron— 3.34—3.15=.19; 3323×.19=	6.3
Net Carbon for Fuel	405.3
Carbon in Gases (based on 54,209 cu ft.)— $54,209\times\frac{13.50}{100}\times.1166\times\frac{3}{11}=$	232.8
$54,209\times\frac{6.4}{100}\times.074\times\frac{3}{7}=$	110.0
	343.8
Carbon in Gases (based on 82,850 cu. ft.)— $82,850\times\frac{13.50}{100}\times.1166\times\frac{3}{11}=$	355.7
$82,850\times\frac{6.4}{100}\times.074\times\frac{3}{7}=$	168.2
	523.9

SHEET XIII. SUMMARY OF HEAT ACTUALLY DEVELOPED AND EXPENDED.

Developed—	Calories.
Combustion of 405.3 lbs. Carbon to CO_2 and CO	1,052,800
Slag Formation	43,096
	1,095,896
Based on Air Received and Gas Analysis	1,029,970
Based on Gas Evolved and Gas Analysis	1,501,300
Expended—	
Melting and Superheating Iron	386,130
Sensible in Escaping Gases	483,150
Retained in Cupola	205,260
Contained in Slag	49,230
Contained in Unmelted Iron	4,800
Contained in Unconsumed Coke	19,850
Lost by Radiation	60
	1,148,480

SHEET XIV. SUMMARY OF EFFICIENCY.

	Calories	%
Heat Required to Melt and Superheat Iron	386,130	24.2
Sensible in Escaping Gases	483,150	30.3
Retained in Cupola	205,260	12.9
Contained in Slag	49,230	3.1
Contained in Unmelted Iron	4,800	.3
Contained in Unconsumed Coke	19,850	1.3
Lost by Radiation	60	...
Latent in Monoxide	444,740	27.9
Heat Accounted for	1,593,220	100.0
Potential Heat by Bomb Determination	1,388,840	
Potential Heat by Analysis	1,498,000	
Per Cent of Iron Wholly Lost		6.4

DISCUSSION OF RESULTS.

Some of the data obtained is susceptible of sufficient accuracy for the purpose required and some is liable to serious error. The figures recorded on the charge sheet (sheet 1) were competently checked over and can be depended upon. The blast data is open to question in several respects; the placing of the Pitot tubes is a delicate adjustment and not easy to detect when out of position. The humidity is assumed dry when as a matter of fact it was high but undetermined. The gas samples stood before analysis and not only could the water absorb gas but the gas was saturated with vapor. The Thwing pyrometer reading is apparently fair but the factor is not vouched for. The chemical analyses of the solids appears correct in nearly every case but inadequate sampling may have precluded obtaining the right figures for the chemical work.

The Pitot tube used in the blast pipe was a Burnham instrument which had been calibrated indirectly against large measured-volume receivers; it was supposed to have been inserted very accurately to .8 of the mean radius of the blast pipe. The Pitot tube in the stack was an instrument made by the author. It consisted of two seamless copper tubes; the static and having a long narrow slot parallel with the flow of gas and the dynamic end circular and cutting sharp and perpendicular toward the entrance. This instrument was previously calibrated against a standardized Burnham instrument and gave almost identical read-

ings. This tube, also, should have been inserted into the stack to .8 of the radius; from the calculated results one or both of the tubes was doubtless seriously displaced.

Fifteen readings with the Thwing pyrometer taken during the run of the previous year, under practically the same conditions averaged 1,126° C. as the observed temperature. This agrees closely with the current observations (1,131° C.), but the factor to be used may be seriously questioned; this investigation has not yet been undertaken.

The gas analyses were made by competent students and indicate very nicely the relative changes which go on during the progress of the run. A continuous sample was taken previous to putting on the blast, this does not enter into any calculations. The sample taken below the charge door came from the immediate vicinity of the wall of the shaft and shows considerable oxygen.

The main gas samples were collected through an opening in the stack about 14 feet above the floor of the cupola; through this same opening a Hoskins fire end determined the temperature of the gases and the Pitot tube recorded their velocity.

Inspection of the summaries indicates that the incoming air may have been somewhat underestimated and the gas evolved much more overestimated. Other than the heat actually developed computed from the stack volumes all the figured amounts agree with each other even better than might be expected.

In all of the short runs made at the Institute it is noticeable that the heat lost by radiation and conduction from the surface of the cupola is practically negligable. In this run the surface of the cupola barely rises above the temperature of the surrounding air; the previous year a portion of the cupola surface was actually lower in temperature than the air of the room.

The sampling of the material is one of the most difficult details of the run. Quite a few of the broken pigs were drilled in several places and the drillings mixed. Sampling the scrap is far more difficult and at best quite unsatisfactory; an effort was made to choose representative pieces and get sufficient drillings from each piece, then mixing for the final sample. To get the composition of the castings four bars were poured at as many different times and these bars drilled and the drillings mixed.

The cupola is conspicuously a very convenient means of remelting and mixing new and used irons for the production of castings. As furnaces go, it is not at all bad in its fuel economy. The more like an iron blast furnace the cupola is driven the greater will be the loss of economy due to monoxide. That is, the greater the heat and consequent rapid melting the more equilibrium is displaced toward the monoxide side; the longer a cupola is run and the more it gets heated up and established in its method of normal running, the greater is the proportional generation of monoxide.

We must thus consider it our own inability rather than any deficiency of the cupola that we get 25 instead of 50 per cent of the heat value from the fuel.

The little Institute cupola is a Whiting No. 0; approximately 19 ins. internal diameter with 2 sq. ft. in the melting section. A 30-in. No. 6 Buffalo forge blower belted to a Sturtevant size 5 motor supplies the blast. In the run just detailed, we have evidently melted 7.1 lbs. iron with 1 lb. fuel; iron has been melted at the rate of 47 lbs. per minute or 23.5 lbs. per sq. ft. of cupola area per minute. This compares well with the results attained by larger cupolas as so admirably tabulated by Stoughton in his text book, and is much better than the rated capacity (1,000 lb. hour).

Considerable better figures would ensue from a longer run or by neglecting the starting-up period.

BELDEN'S EXPERIMENTS.

Several features of the recently issued bulletin of the Bureau of Mines on "Foundry-Cupola Gases and Temperatures," by A. W. Belden, present startling conclusions, from our point of view.

Belden was unable to get results with a fan blower and discarded it for a rotary impeller type.

In view of the particular adaptability of fan blowers to the pressures and capacities required by cupolas, and although Belden demanded nothing not desired by the usual foundryman, they will likely survive such heavy condemnation. Any blast equipment must be kept in good and uniform condition and it is not so clearly apparent as to just why a fan blower cannot be used satisfactorily.

The Pitot tube is commonly used to determine and transmit the static and dynamic pressures to a gauge which shall determine their difference. On the difference of these two pressures we base our calculations for gas velocity and volume; the accuracy of the method we believe pretty well established. Belden connects his Pitot tube to a simple manometer and gets some 5.3 ounces as his average pressure during a run. He does not say whether this is static or dynamic head; it is hardly the difference, the only value which it is necessary to use such a refined instrument as the Pitot tube to measure. It would be interesting to learn just what was measured by his instrument.

Belden does not mention any determination of moisture in his gas analyses nor does he speak of its influences on operations.

The Bureau of Mines' tests were made to cover a period of 15 minutes after the blast had been on already 15 minutes. In view of the well-established fact that conditions inside are changing materially during the run and that after a couple of hours the relative amounts of dioxide and monoxide may be practically reversed, it appears woefully incomplete to choose any one 15-minute period and confine investigations to that range.

Most astounding of all is Belden's placid entire omission of iron in his investigations and then in his conclusions discussing practically nothing but the melt-

ing of iron. That he has made a good many useful and important determinations goes without saying; that his experiments can replace runs *with* iron is an entirely unwarranted assumption.

His conclusions, although emanating from so austere a source as the Bureau of Mines, would read quite as glibly if he had done no investigating whatever. His "ideal melting region" as the line of highest carbon dioxide content together with an absence of oxygen fits well with the next sentence that best results will be obtained by melting in the region of highest temperature together with absence of oxygen and the third sentence after that: "Experimental determination of this region is not necessary."

After Belden's pioneer attempts the Bureau ought to be in position to make some complete investigations and in particular give us some information about how to improve the efficiency of the cupola.

For many years North Carolina has been the largest producer of mica in the United States, according to the United States Geological Survey. Prior to 1895 the output came chiefly from the larger mines and consisted of big sheets of fine quality. At that time large quantities of small sheet mica that would cut plates less than 3 ins. square were thrown on the dumps as waste. After the small sheet and scrap mica became valuable, the dumps at the large mines were worked over and the quantity of mica produced was thereby greatly increased. Now that most of the dumps have been worked over and only a few large mines are in operation, the output is barely maintained by a large number of small mines and prospects, probably as many as a hundred. Many of these are worked by the mountaineer farmer and miner at times when crops are laid by, and occasionally one of the prospects develops into a large deposit.

The gross value of Colorado's output of gold, silver, copper, lead, and zinc recovered from placers, from gold-silver bullion, and from ore sold or treated in 1912, was $37,320,966, as compared with $32,418,218 in 1911, an increase in value for 1912 of $4,902,748, or 15 per cent, according to Charles W. Henderson, of the United States Geological Survey. These figures are compiled and tabulated strictly as a mine report and with reference to the locality of each individual mine, and not with reference to the locality of the shipping point of the product. The production of gold in Colorado in 1912 showed a decrease in value of $413,413; of silver, an increase of 881,902 ozs.; of copper, a decrease of 917,185 lbs.; of lead, an increase of 5,562,978 lbs.; and of zinc (figured as spelter and zinc in zinc oxide) an increase of 37,615,356 lbs. With increased market prices for silver, copper, and zinc, there were increases in value of $160,644 for copper, $1,165,434 for silver, $250,334 for lead, and $3,730,749 for zinc.

THE USE OF LIME IN CYANIDE WORK.*

By A. M. MERTON.

Text books on cyanide practice usually treat the question of lime consumption and the addition of lime to the ore in a very casual manner. It appears to be accepted generally that, if the solutions in the percolating and agitating vats are alkaline, the lime has effectively done its work. That is probably the case when the ore is crushed in water, but the now almost universally used process of crushing in cyanide solution and reducing the ore to a mill slime has introduced new metallurgical problems, not the least of which is the mode of adding the lime to the ore. The fact seems to have escaped the authors of text books that lime may be added to an ore in exactly the amount shown by tests and the solutions going to percolators or agitators may have just the right degree of alkalinity, yet, at some point during the process of crushing a great percentage of the pulp may be acid, with a resulting loss of cyanide.

Few mill designers make provision in their plans for the convenient handling of lime in the mill nor adequate arrangements for the addition of the necessary amount of lime to the ore. A shovel or an old box is the sum total of the lime handling machinery at many a pretentious mill.

The lime item shows up in a cyanide mill cost account as one of the heavy charges. There are cases in which the expense for lime is even greater than the combined cost of cyanide and zinc. The consumption of lime is especially high in cyaniding silver ores. The following figures show the consumption in some of the principal Mexican districts and plants: Dos Estrellas mill, 28 lbs. per ton of ore; Pachuca district, 20 to 24 lbs. per ton; Guanajuato district, 18 to 22 lbs. per ton.

In Mexico lime is generally cheap but, both in that country and in the United States, it may reach 1 cent per pound delivered in the mill bin. The lime bill per month can be a very important sum. The matter is worth more than the slight attention often given to it and it is of some moment in mill economics to make an investigation into whether the lime used is fulfilling its function to the uttermost.

Lime performs many functions. Thus: (1) Neutralizes acids formed by the oxidation of sulphides, etc.; (2) breaks up metallic salts forming innocuous hydrates; (3) protects the solution of cyanide against carbonic acid; (4) furnishes the alkali necessary for the breaking up of silver minerals; (5) protects the solution against the latent cyanicides in the ore.

The effect of actions 1 and 2, and to a certain extent 5, becomes most apparent during the crushing and grinding of the ore. The amount of lime to be added for these purposes can be determined in the laboratory. The amount of "protective" alkalinity

*From Mining Science.

to be carried in the solution depends upon conditions in the mill and must be found experimentally. So far as the degree of alkalinity required by silver ores is concerned, it may be stated that it is usual to have practically at all times a concentrated lime solution. At Pachuca, for example, the pulp in the agitators carries a slight excess of solid lime, so that, as the lime in solution is used up, it is restored by dissolving some of the calcium hydrate in the pulp. The lime losses are therefore made up as follows: (1) Lime consuming constituents in the ore; (2) lime destroyed by CO_2 in the air used in agitating; (3) mechanical loss by solution passing out of the mill system with the tailing.

It would unduly extend the scope of this article to consider in detail all the functions of lime and the losses due to causes (2) and (3) just given. In passing it may be stated that the tremendous volumes of compressed air now used in cyanide plants contain very considerable percentages of CO_2, due to the decomposition of lubricants used in the cylinders of the compressors. If compressed air is bubbled through a clear alkaline mill solution a cloudy precipitate of calcium carbonate will soon make its appearance and shortly its effect on the cyanide will become apparent. Care in the choice and use of compressor lubricants and perhaps a purification of the compressed air will be well repaid.

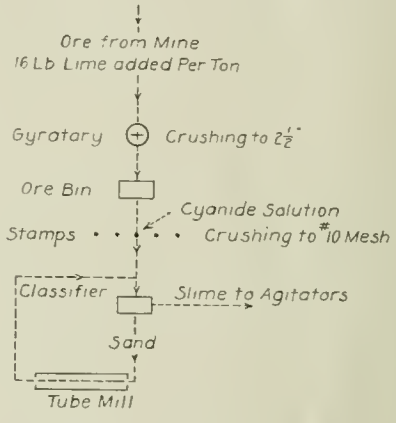
The main object of this article is to call attention to a point overlooked in the general literature of cyanidation, although well understood by many cyanide operators. The point is that the mere addition of lime to the ore, in quantities called for by test, will not suffice to protect the cyanide solutions, even in spite of the fact that the solutions and pulp running to the agitators from the crushers may be quite alkaline.

Not so very long ago practically all ores were crushed in water, amalgamated, the sands and slimes separated, the sands treated in percolators and the slimes either thrown away into dams or given a perfunctory treatment. Then, the sands having been washed with water, contained almost no acid and a little lime added to the sands or even just sprinkled over the surface of the vat charge fully sufficed.

Now, however, the all-sliming process has become almost the standard process. The ore is crushed in cyanide solution so that almost all passes a 200-mesh screen. During the crushing the solution must at all times be protected against the action of cyanides in the ore and thus the old hit-or-miss style of adding lime must be abandoned or unduly large losses of cyanide will be made.

Take, for example, the conditions illustrated in the accompanying flow sheet. The diagram shows a typical "all-sliming" crushing and grinding plant working in cyanide solution. The ore consumes 16 pounds of lime per ton and the plup going to the agitators is continuously alkaline. Yet there is a heavy consumption of cyanide, hastily, and erroneously, attributed to the action of soluble minerals in the ore. The fact was that, roughly speaking, from one-third to one-half the ore was being ground in an acid solution. By adding lime to the tube mill and cutting down the amount of lime fed to the ore before the gyratory crusher, the cyanide loss in the crushing circuit was reduced to one-half.

In such a circuit as that illustrated the conditions calling for the addition of lime will be difficult at each crushing stage. For example, at the gyratory crusher only a small portion of the lime can be used owing to the coarseness of the ore. Yet tests of the fines disclosed the fact that they required much more lime (per ton of fines) than the general average of the



Flow of Ore in Crushing Circuit.

ore. This was due to the presence of vugs, many of which contained soft, partly decomposed and intensely acid sulphides. The ore may lie in the bin 24 hours before crushing in the stamps. The natural moisture in the ore will generally slack the lime. Under the action of the stamps most of the lime will be converted into milk of lime, washing and neutralizing the acid on the outside of each ore particle. A few chips of lime will escape with the 10-mesh ore. On passing to the classifier the portion of the ore already fine enough will pass away together with most of the lime in solution. The sands, containing a higher percentage of sulphides than the original ore, will go to the tube mill with a deficiency of solid lime. The pulp fed to the tube mill will contain only about 40 per cent of solution and this will not be sufficiently alkaline to protect itself against the acid in the great excess of ore. Thus it is inevitable, in many cases, that the tube mill will discharge an acid product, which on being returned to the classifier will be neutralized by the excess of lime in the stamp mill discharge. Under such conditions I have found as high a loss as 50 per cent of the cyanide in the solution fed to the tube mill.

In considering the question of acidity it would seem, at first sight, that the action of the acid would be to form only hydrocyanic acid and that by the addition of lime the titratable cyanide would be entirely restored to the solution. Experience is against

that opinion. Cyanide is a chemical compound that tends to break up into a multiplicity of chemical bodies. Even the simplest reactions have an efficiency of only 80 per cent, or so, the remaining 20 per cent going into cyanogen, ammonium compounds, complex organic compounds, etc. In mill solutions the conditions are worse owing to their complex nature. These considerations demand that, in order to economize cyanide in mill solutions, the entire mill circuit must at all times and at all points be kept neutral or at least slightly alkaline.

In a silver mill the lime conditions are slightly better than in a gold mill, owing to the strongly alkaline solutions used in the former mill. Gold mills usually carry the solutions near the neutral point or at best only very slightly alkaline.

The lime conditions in the all-sliming circuit illustrated are worthy of further study. It was found by investigation that the lime was consumed unequally at different points in the circuit. The requirements at different points were as follows:

At breaker—pounds lime per ton of ore milled	3
At stamps—pounds lime per ton of ore milled	9
At tube mill—pounds lime per tone of ore milled	4
Total	16

Clearly, in order to get correct lime conditions in each part of the circuit it is necessary to have those amounts (as shown above) present at every stage. From considerations already discussed it is obviously impossible to obtain correct conditions by adding lime at the commencement of the circuit. Thus, in the case used as an example, the tube mill discharge required three pounds of lime to neutralize the acid developed by grinding in the mill. In other words, 16 lbs. of lime were used and only about 14 lbs. were really useful.

To add lime correctly, that is in such a manner as to keep the solutions at all times protected against cyanides, it is necessary to add those amounts of lime such as are consumed by the ore at each stage of the circuit. Thus, in the case in question, by adding 12 to 14 lbs. of lime to the ton of ore as it comes into the mill and from 2 to 4 lbs. to the tube mill feed, at no stage of the crushing will the pulp run acid.

However, in milling, the heterogeneous nature of ores from even one mine is soon apparent. Every part of the mine seems to produce a different kind of ore. It is even worse in treating a dump. The mill man has a constantly fluctuating character of material to deal with. Thus, an ore which requires a daily average of 12 lbs. of lime per ton, may be made up of lots of ore requiring respectively 6, 8, 14, 16, 18 lbs. of lime. The lots may be large or small, coming regularly or the reverse, according to the exigencies at the mine. Yet the mill has to receive the ores as they come and in most cases without any provisions being made to equalize conditions. Ores do not mix very much as they go through the crushing system, except perhaps in a large mill. In a mill of 200 tons capacity it is usually the case that a lot of 20 tons will go through the mill with very little mixture with preceding or following lots. In a large plant, say a 60-stamp mill crushing 800 tons daily, a 20-ton lot would be divided between six large bins, probably by a belt distributor, say three tons to a bin. Such a small quantity would lose its identity in such large bins and thus a pretty effective mixing would result. In a 10-stamp mill such a lot would about one-quarter fill a bin and would go through the stamps with very slight admixture with other lots. If an insufficient amount of lime were added to such a lot trouble would ensue in the mill. This is an example which shows that it is sometimes easier to run a large mill than a small mill.

The most satisfactory remedy for such a condition of affairs is to "bed" the ores, thus converting a very heterogeneous mass into a nearly uniform mixture. This is the plan now being adopted by a large mill in Mexico. It is also adopted in the Golden Cycle mill at Colorado City. However, few non-technical managers will allow the metallurgist to adopt such a scheme. A little team work between the mine and mill superintendents will, however, accomplish a great deal in this respect. By having a few bins at the mine, each for a special part of the mine, it is possible for the metallurgist to make a rough classification of the ores. By drawing off from each bin separately and by adding a little less than the amount of lime shown by laboratory test as required per ton of ore, the main difficulties will disappear. The lime may be added by measure to the top of every car sent to the mill, or in case a conveyor is used an adjustable lime feeder may be employed. In the latter case a lime crusher will be required.

By the exercise of some ingenuity the mill superintendent can often effect a fair degree of mixing even in the mill bins and no opportunity should be lost in a small plant to mix the ores. By so doing the handling of the solutions will be greatly simplified and important economies effected in chemicals.

CHARACTERISTICS OF LIME.

Not only is the ore a very irregular material but the lime used will vary greatly in strength. Different consignments of lime may have a very varying value as a neutralizing agent, although fortunately each lot is usually very uniform. Especially in Mexico, where small kilns are used, the lime is likely to be very irregularly burned. Lime is valuable only for the calcium oxide (CaO) it contains. The percentage will depend on the quality of the lime rock used and the temperature and time of burning. Lime burners are not above running in a lot of inferior lime and every new lot purchased should be sampled and tested.

On the receipt of a consignment of lime at a mill, it should be inspected, sampled and tested. Different lots at the same mill during a year may show the following amounts of lime required to neutralize the acid in a standard ore sample: 6, 13, 9, 8, 7, 12 lbs. per ton of the same ore. That is, lot No. 2 was worth less than one-half per pound that of lot No. 1. Lime, for cyanide work, should be purchased strictly on the basis of the percentage of available lime.

Lime in large quantities and which has to be stored for long periods should be free from an undue quantity of smalls. It goes without saying that the lime must be free from charcoal, coke, charred wood, etc., as these tend to reprecipitate dissolved gold and silver.

DETERMINATION OF AVAILABLE LIME.

The test used for many years differs slightly from that recommended by the Mine Trials Committee. A stronger sugar solution gives quicker results and with a correctness well within that of the method of sampling.

Weigh out 2 grams of a lime sample crushed to a 60-mesh screen. Pour into a litre flask. Add 50 grams of crystallized sugar and about 800 c. c. water. Shake thoroughly a few minutes and allow to stand for a couple of hours with occasional shaking. Make up to 1,000 c. c. and shake. Take out 50 or 100 c. c. with a pipette and titrate with standard oxalic acid using phenolphthalein as an indicator.

Standard oxalic acid. Oxalic acid is now generally used in cyanide plants for the determination of alkalinity owing to the ease with which the standard solution can be prepared. By dissolving 22.5 grams of the crystallized acid in 1,000 c. c. of water, 1 c. c. = 0.01 grams CaO. The crystals of oxalic acid contain two molecules of water and they are constant enough in composition to allow a standard solution to be prepared directly by weighing. Where very great accuracy is required the solution can be standardized against chemically pure lime.

The following data on lime may be valuable to mill men and chemists:

SOLUBILITY OF LIME IN WATER.

Temp. ° C.	CaO in Saturated Solution.
10	0.128%
15	0.124%
20	0.120%
25	0.115%

PERCENTAGE OF CaO IN MILK OF LIME.

Sp. Gr.	% CaO
1.01	1.15
1.05	6.10
1.10	11.45
1.15	16.70
1.20	21.25
1.25	25.80

SOLUBILITY OF CaO IN SUGAR.

Sugar in 100 c. c.s Water.	Sp. Gr. on Saturation with CaO.	CaO in 100 c. c. of Syrup.
40 grams	1.179	10.6 grams
30 grams	1.148	7.5 grams
20 grams	1.104	4.7 grams
10 grams	1.053	2.2 grams
5 grams	1.026	0.9 grams
0 grams	1.000	0.12 grams

Lime (CaO) is also very soluble in solutions of glycerine.

STORAGE OF LIME.

Many mills have been destroyed by fires starting from the lime house. The shed used for lime storage should be built of fireproof material and thoroughly proof against moisture. Lime should not lie on an earth floor. A satisfactory floor may be built by laying down corrugated iron sheets on a rough board floor raised eight or nine inches above the ground. The iron sheets should be well lapped to prevent any lime working through to the wood. In case a frame building is used both sides and ceiling should be covered with corrugated iron well lapped and closely nailed. Treat lime as a dangerous body.

It is expected that sugar cane in Argentina this season will yield 200,000 tons of sugar, the largest crop this country has had.

The important deposits of phosphate rock in Algeria have been developed during the past 15 years, production having increased from 1,057 short tons in 1899 to 550,000 tons in 1912. The two mineral zones or districts in which it is mined are near the towns of Setif and Tebessa. The Algerian deposits are a continuation of the important deposits of Tunis. Algerian mining companies sell their phosphate rock c. i. f. at the important European markets at prices which were on July 4, 1913, as follows: For 63 to 68 per cent phosphate, at British ports, and Hamburg, 11⅓ cts.; Italian ports, 11 1/5 cts.; Antwerp, 11 6/10 cts. For the 58 to 63 per cent phosphate the prices at these respective places were 11 cts., 10 8/10 cts. and 10 8/10 cts. Sales are on the metric ton (2,204.6 lbs.) basis and the price is obtained by multiplying the percentage of phosphate in rock by the current rate paid. Thus the price in Great Britain for rock containing 65 per cent of phosphate would be $7.37 per ton.

The great magnitude of the clay-working industry of the United States is shown in a chart just issued, compiled by Jefferson Middleton, of the United States Geological Survey. This chart shows a total value for 1912 of $172,811,275, which is an increase of $10,575,094 over the figures for 1911. These products include the several varieties of brick, drain and other tile, sewer pipe, terra cotta, pottery, fire brick, and other clay products, the various building bricks representing the greatest value, with a total of $73,425,819. The number of building brick manufactured was 10,281,114,000. Ohio led the states in the value of her clay products with an output amounting to $34,811,508, or over one-fifth the total production for the United States. Pennsylvania was second, with a production valued at $21,537,221; New Jersey third, with $19,838,533; and Illinois fourth, with $15,210,990. Eight states produced clay products in 1912 to a value exceeding $5,000,000 and 26 states to a value exceeding $1,000,000.

THE LABORATORY

METHODS OF ANALYSIS USED IN THE LABORATORIES OF THE ARMOUR INSTITUTE OF TECHNOLOGY.

The Milling of Wheat and the Testing of Flour.

The grading of wheat for purchase and sale has been, and is to a very great extent, a matter of optical inspection by an expert trained through experience rather than of accurate scientific data. This results in a certain amount of confusion and of argument between buyer and seller, each of whom is acting upon an opinion as to the grade of the product, and if a disinterested party is called upon he can furnish only an opinion.

This situation has resulted in a call upon the chemist upon the part of some of the larger millers and wheat traders in an attempt to put the grading of wheat upon a scientific basis as to yield and quality of flour, chemical composition, and actual performance in the baking of bread.

There are at present a number of laboratories in which wheat milling, grain and flour analysis, and baking tests are carried out. Some of these are in connection with commercial laboratories, and some with millers and wheat traders.

The general procedure in the above tests is common to all, but there is a great deal of difference with details of the various processes. These differences result in various laboratories failing to agree in their reports upon the same material, since the differences between the grades of wheat and flour are, in many cases so small as to be upset by variation in conditions of milling and testing.

This matter is not so serious as it at first appears, for the tests are made in general, upon the basis of comparison between various samples and with a standard material, and while different laboratories might fail to agree upon a single sample, they would agree well as to the grading of a number of samples.

It is to be hoped that there may be, in time, official methods standard as to detailed procedure, for the milling, chemical testing, and the bake testing of wheat and flour.

Until this time comes the following methods are suggested as giving satisfactory results:

The Milling Test.—The milling equipment consists of a special Allis-Chalmers Experimental Mill comprising three sets of six-inch rolls and a jig bolting machine. Two sets of the rolls are corrugated; one set 10 and 12 to the inch and the other 24 and 18 to the inch. These rolls grind dull to sharp and the fast roll runs a little more than twice as fast as the slow one. The smooth rolls have a differential of 7 to 10, that is, the fast roll makes 10 revolutions while the slow one makes 7. Accurate adjustment of the rolls is provided by two large screws on the side of each roll, which allow the rolls to be adjusted so that they are in the same plane, and by two smaller screws to set them parallel. The rolls are thrown "in" and "out" by means of a lever. A mechanical jig bolting machine completes the equipment of the mill. Frames of standard bolting cloths are made to fit this jig and as many as four frames may be inserted at one time.

Before going to the mill the wheat must be clean, as that term is ordinarily understood. This is usually accomplished by the use of some sort of fanning mill, which does not, however, remove much dirt from the crease. In this laboratory a Eureka Horizontal Close Scourer, manufactured by the S. Howes Co. was used. It removes the crease dirt, a considerable portion of the outer bran coat, and the beard from the end of the kernel. The scourer is capable of wide adjustment to suit various sizes of stock, and this particular machine was built to scour as closely as possible and also to deliver *all* the product at the exit openings of the scourer, leaving no residual material to contaminate the succeeding sample. A sufficient quantity of wheat, usually 1,200 grams, is weighed out for scouring. The loss in scouring is determined and 1,000 grams of this cleaned wheat is weighed out for the milling.

Any successful milling of a wheat requires the very gradual reduction of the wheat to flour and it is in this gradual reduction that the experimental mill falls short of what may be accomplished with a commercial milling equipment. At the same time, the experimental milling must follow along the same lines as the commercial milling if the flour obtained is to accurately represent the flour-producing value of the wheat.

A somewhat extended line of experiments convinced us that it is necessary to decide for each variety of wheat approximately the quantity of straight flour we desire to produce from it and then mill in such a manner as to produce the very best flour possible from the wheat and of the percentage previously determined. Different varieties of wheat are ca-

pable of producing different quantities of first class straight flour and any attempt to produce more than this percentage of flour from these wheats will at once lower the quality of the flour secured.

Our experimental work convinced us that the Northern Spring wheats gave the best straight flour when milled to produce about 66 per cent of product. Hard Winter wheats produced the best flour when milled to about 63 per cent of straight flour. Soft Winter wheats should not be milled to produce in excess of about 58 per cent of straight flour. A more intensive milling of any of these wheats leads at once to a marked reduction in color and also to an increase in the percentage of ash, both showing that bran particles are finding their way into the flour.

The adjustment of the rolls in the experimental mill will be determined by the size of the wheat kernels being milled. The wheat should pass through the rolls set first so that the wheat kernels will be cracked and this as lightly as possible. They should then be brought closer and closer together until they finally run almost touching as the wheat receives its final milling on this set of rolls. After each passage through the rolls, the product goes to the sieves. Our customary arrangement of the sieve is to place at the bottom of the jig a number eleven flour sieve, on top of this a No. 34 bran sieve and on top of this a No. 16 or No. 18 coarse bran sieve. In the first set of rolls only the product remaining on the upper sieve is remilled. When the milling has been completed on the first set of rolls, which will be accomplished in about 6 or 7 passes, the material remaining on both of the bran sieves is passed to the second set of rolls. About three passes on these will be sufficient. The material from both the first and second bran sieves is then weighed up and discarded from further milling operations. Up to this time, only a very small percentage of flour has been produced and found its way from the flour sieve to the receptacle provided for it. The material remaining on the flour sieve then passes to the smooth rolls for final milling. In our laboratory, it is customary to pass the material from the smooth rolls eight times with sieving between each passage and with the space between the smooth rolls being made smaller and smaller. Practically all of the flour is produced in this milling on the smooth rolls. The material remaining on the flour sieve after this milling is weighed up and discarded. The material, which has passed through the flour sieve is resifted through a No. 13 flour sieve to remove some of the bran particles and dirt which may have escaped the No. 11 sieve and weighed to give the percentage of flour produced.

The flour produced in this way should be very uniform in texture and color, and should be entirely free from any specks of bran or dirt.

The flour thus produced will compare very favorably with the straight flour produced in any commercial mill. It will, of course, not be equal to the patent flour marketed from a commercial mill, as this patent flour is made by taking the straight flour milled and by subjecting it to a system of air separation and sieving to remove much of the bran particles and some of the germ, which otherwise finds its way into the straight flour. The patent flour will vary all the way from 45 per cent to 90 per cent of the straight flour milled.

The milling description, which has been given, applies to wheats which have recently been harvested and which contain their normal moisture content. In case the wheat has been harvested for some months and has lost a considerable percentage of its normal moisture, it is necessary to add water to the wheat and allow this water to be taken up by the wheat before milling. This process is known as tempering and is for the purpose of softening the bran layers so that they will flatten out in the rolls instead of cutting up.

The above methods of milling are stated because they are the ones we found best, although we do not believe it impossible to improve on them. They are suggested for use until better ones are devised and until the various laboratories can agree on a common method of milling.

Chemical Analysis of the Flour.—The determinations made in the chemical analysis of the flour are: Moisture, ash, total nitrogen and on some samples, gliadin nitrogen.

All flour samples should be weighed by difference from glass weighing bottles to guard against the loss or gain of weight due to the condition of the air.

Moisture.—A sample of about two grams is weighed by difference into a glass tube (¾ inch by 3 inches) closed at one end and made to fit closely into another similar tube which is weighed with it. The sample, in the first tube, is heated for seven hours in the air, at a temperature of 103° C., when it is slipped quickly into the other tube and the whole cooled in a dessicator and finally weighed. Loss in weight is moisture. The telescoping weighing tube is used because the dried flour is highly hydroscopic.

Moisture tests upon whole wheat are made by means of the Brown and Duvel Moisture Tester as adopted by the U. S. Department of Agriculture. This consists essentially of a set of stills heated by gas in which 100 gms. of wheat is placed and covered with a non-volatile oil. Heat is applied for a period of several hours, all the water being distilled off and caught in a graduated cylinder. The volume in cubic centimeters is the percentage. The apparatus may be obtained from the Kuy Scheerer Company of New York.

Ash.—A 5-gram sample of flour is weighed into a platinum dish and burned in a muffle, slowly at first, at a low heat and finally at a bright red heat.

Total Nitrogen Calculated as Protein.—A combination of the official Kjeldahl and Gunning methods is

used, for which the following solutions and reagents are required:

1st. Accurately standardized solutions of HCl and NH_3 are required. These solutions should be exactly equivalent to one another, volume for volume, and the HCl should be of such strength that each cc. of it is equivalent to 1 per cent proteid when a 2-gram sample of flour is taken for analysis. The percentage of nitrogen multiplied by the constant 5.7 gives the percentage of proteid. To get a solution of HCl of the desired strength, a solution of a little more than quarter normal strength (about 9.3 gm. per litre) is made up from concentrated hydrochloric acid and water. After thorough mixing, this solution is accurately standardized by precipitation of the chlorine as AgCl by $AgNO_3$ and weighing AgCl on a Gooch crucible. The strength of HCl desired is calculated in the following manner:

Since 1 cc. is to equal 1 per cent on a 2-gram sample, then 100 cc. would equal 100 per cent or 2 gms. of proteid.

Since nitrogen $\times$ 5.7 = proteid, then 2 gm. proteid $= \frac{2}{5.7} = 0.3509$ gm. nitrogen.

Now $NH_3 + HCl > NH_4Cl$ so 1 N equivalent to 1 HCl and from the proportion:

1 HCl : 1 N :: $\times$: 0.3509, or

36.5 : 14 :: $\times$: 0.3509 and $\times = 0.9148$,

we get 100 cc. HCl solution, equivalent to 2 gms. proteid, or 0.3509 gm. nitrogen, contains 0.9148 gm. HCl, and 1 cc. contains 0.009148 gm. HCl.

The standard solution prepared as above, and having a standard a *little greater* than 0.009148 gm. per cc. must now be diluted to the correct strength. The number of cc. to be added to each litre of the stronger solution, is calculated as follows: .009148 : standard as determined :: 1,000 : $\times$ — 1,000 = number of cc. water to be added to each litre in order that the solution may have the required standard. The measurements of solution and of the volume of water to be added should be made very carefully, and after thorough mixing, the solution should be restandardized.

If the standard is not exactly right, another dilution should be made and the standardization repeated until the desired result is obtained.

The ammonia solution is now prepared, and diluted until it exactly matches the acid volume for volume.

In all titrations lacmoid is recommended as an indicator.

Pure sulphuric acid, sp. gr. 1.84, a saturated solution of NaOH, a solution of potassium sulphide, 40 grams, per litre, powdered potassium sulphate, pure mercury, and some small lumps of pumice stone are also required.

Upon these reagents blank determinations should be made to make sure that all are nitrogen free, or to provide a constant correction.

Procedure.—A 2 gram sample of flour is placed in the Kjeldahl digestion flask (used also for the distillation) where it is mixed with 10 gms. K_2SO_4 and 0.66 gm. of mercury, and 25 cc. of conc. H_2SO_4 added. The mixture is heated gently until frothing ceases, and then digested at the full heat of the naked bunsen flame until colorless or nearly so, and a short time after that point is reached. This should require less than two hours, a much shorter time than either of the official methods.

When the digestion is complete, the flask and contents are allowed to cool, and the solution diluted to 200 cc., a few pieces of pumice being added to prevent bumping and 25 cc. of K_2S solution to precipitate the mercury. The acid is then neutralized and the ammonia liberated by the addition of 60 cc. of the strong alkali solution, the solution being poured down the side of the inclined flask so that it may not mix with the acid solution. The flask is connected with the block tin condenser by means of a Hopkins bulb tube to prevent any of the alkali solution from being carried over mechanically, and the end of the delivery tube of the condenser placed under the surface of 40 cc. of the standard acid in an Erlenmeyer flask. When all is ready, the distillation flask is rotated to mix the solutions, and heat applied. The whole is boiled briskly until about 150 cc. of distillate has passed over, this being sufficient to assure the elimination of all ammonia. At this point the delivery tube is disconnected, the flask removed and its contents titrated with the standard alkali. The net volume of acid solution equals per cent nitrogenous compounds.

It is sometimes desirable to determine the percentage of gliadin. This is done as follows: *One gram of flour is extracted with 100 cc. of 75 per cent alcohol, by shaking the mixture thoroughly in a flask and heating for an hour at a temperature just below the boiling point of alcohol, with occasional shaking. After standing for an hour the hot liquid is decanted upon a 10 cm. filter and 25 cc. of the hot alcohol are added to the residue and shaken, after which the residue is again allowed to settle and the liquid decanted. This is repeated six times. The remainder of the alcohol is then driven off by evaporation and the nitrogen determined in the residue by the method described for total nitrogen.

The number of cc. of HCl used is the percentage of gliadin. The ratio $\frac{\text{Gliadin}}{\text{Total protein}}$ is called the gliadin ratio, and in general the larger this number, the better the quality of the flour.

These determinations are made use of in a valuation of a flour about as follows: The ash tells us in a rough way about how much of the bran has found its way into the straight flour milled, as the patent

*Leach, "Food Inspection and Analysis," p. 299.

flours have the lowest ash of any on the market. The patent flours made from the different varieties of wheat have somewhat nearly a constant ash and by comparing the ash of our straight flours with those of the patent flours obtained from corresponding varieties of wheat, we have a measure of the value of a wheat which is being tested for its production of patent flour.

The moisture determination is used in calculating all of the samples tested to a constant basis of moisture content. It is also used in calculating the quantity of water absorbed by the flour in the preparation of a dough of standard consistency.

The nitrogen determination is on the same basis as the ash determination. It is a comparison between the nitrogen of the straight flour and that of the patent flour prepared from the same varieties of wheat. As the nitrogen on the whole wheat is higher than that in either the straight flour or the patent flour prepared from it, the value of the wheat as a source of patent flour, varies inversely as the ratio between nitrogen in straight flour and nitrogen in patent flour.

The determination of gliadin nitrogen is made in order to compute the ratio between total nitrogen and gliadin nitrogen. In general, the higher this raito the higher is the quality of the flour. Whole wheat flour having the lowest gliadin number and a constantly increasing ratio from the whole wheat up to the patent flour.

(To be continued).

The Isthmian Canal Commission has awarded contracts for an oil-burning furnace for annealing various sizes and kinds of steel castings; another furnace for drying molds for steel castings; also for four oil-burning ovens, one for drying large cores for steel, iron, and brass castings, and three for drying smaller cores. These are all to be installed in the new foundry building at Balboa and will cost $13,740.

The manufacture of pottery is one of the most important branches of the clay-working industry in the United States. During the year 1912 pottery was produced to the value of $36,504,164, according to the annual chart just issued by the United States Geological Survey, showing the production of all clay products, compiled by Jefferson Middleton. This figure indicates a healthy condition of the pottery industry, the increased value of the output for 1912 over 1911 being almost $2,000,000. Ohio was by far the largest producer in 1912, being credited with $15,508,735, and New Jersey was next, with over $8,000,000. Six states produced pottery to the value of more than $1,000,000.

THE CHEMICAL EXAMINATION OF LIQUID FUELS.*

By W. HAMILTON PATTERSON, M.SC.

In comparison with the enormous advances made in the mechanical application of oil as a source of power, the chemical side of the question has been somewhat neglected, and there is much room for scientific research and investigation in the preparation and utilization of fuels. There is also much overlapping and ambiguity in the nomenclature of the various technical products which are put on the market as liquid fuels. There should be some distinction between "oil fuels" and "fuel oils." In this paper the term "fuel oil" will be reserved for oils burnt in external combustion, e. g., under a boiler for the purpose of raising steam; "oil fuels," on the other hand, will mean oils utilized for the production of power in internal combustion engines. The term liquid fuel may be applied in either case.

Although many fuel oils may often be equally well utilized as oil fuels, there is a difference in the requirements. In oil fuels volatility is of greater importance, and the obtaining of oils which will neither corrode nor give trouble in the cylinders of internal combustion engines on explosion or burning. In fuel oils more vital factors are cheapness, a fairly high flash point, and high calorific value. The various liquid fuels and their allied products derived either from petroleum or coal tars are not definite compounds; it is therefore impossible to assign to these varying mixtures scientific names. It is, however, greatly to be deplored that, in technical usage, the same name is not applied in different parts of the world to denote what is essentially one and the same product. What confusion occurs, for example, in the meaning of the words paraffin, benzine, solar oil, naphtha, etc. To add still further to the chaos which already exists, we find specially coined trade names. Of oil fuels the only variety widely used for certain kinds of motor engines is petrol, but alcohol might be used instead with equal efficiency, provided it could be obtained cheaply enough, and also benzol, or, even better, a mixture of the two.

When, however, liquid fuels have to compete with coal for the production of power, only crude products, by-products, or residues can be considered. The available sources of such liquid fuels may be divided as follows:

(1) Crude petroleum or residues and products from petroleum.

(2) Tar oils from coal distillation, coking or producer plants, especially from bituminous coal producers.

(3) Liquids or oils from vegetable or animal sources, including alcohol and nut oils (at the present time of little importance).

*From Journal of the Society of Chemical Industry.

(4) Oils from lignite, peat, wood, or shale.

The last class is not very important as far as this country is concerned, except as regards the Scottish oil production from shale, which amounts to about 70 million gallons per annum. This figure includes, however, a large percentage of constituents too valuable to be utilized as ordinary liquid fuel. The following results have been obtained in the examination of various liquid fuels, most of which are available in this country and obtainable at the cheapest price; the highest price (i. e., at the time of the experiments) in any case in this country being a little over £3 per ton, most of them, however, being considerably cheaper. They have been examined more particularly with reference to their use as oil fuels. The calorific values were determined by the Mahler bomb calorimeter, a method which gives absolutely reliable results when worked under proper conditions. The oils tabulated would give an efficiency proportional to their net calorific value. It will further be seen that the sulphur content is in no case excessive. The much lower calorific values of oils Nos. 16 and 17 may account in some measure for the trouble they give in Diesel engines, but there are other factors which are brought out in the tables below. In combustion of fuels in the bomb calorimeter, the products of combustion are cooled to the ordinary temperature of the calorimeter; the hydrogen of the fuel is oxidized to water which gives up its latent heat on condensation. There is also a small amount of sulphuric and nitric acids produced which must be allowed for. The heat value actually obtained in the bomb calorimeter is the gross value, while that corrected for hydrogen and acid formation is the net value, and corresponds to the maximum energy of the fuel which is available for the production of

TABLE I.

No.	Description.	Sp. gr. at 15-OC	Carbon	Hydrogen	Sulphur	Oxygen and Nitrogen	Net calorific value in calories	Net calorific value in B. Th. U.
1.	Fuel oil used on trial of a torpedo destroyer...	0.921	85.28	11.93	0.55	2.24	9,986	17,975
2.	Petroleum product sold at a little over £2 per ton	(0.888) at 18° C.	86.20	12.57	0.31	0.92	10,097	18,175
3.	Ordinary crude petroleum.....	0.923	.....	.....	0.45	....	9,956 (Hydrogen assumed 12.0%)	17,921
4.	"Light fuel oil".....	(0.900) at 18° C.	85.58	10.81	0.43	0.18	10,114	18,205
5.	"Admiralty fuel oil".....	0.928	86.40	11.55	0.34	1.71	9,961	17,930
6.	"Residum"	(0.943) at 18° C.	86.44	11.23	0.30	2.03	10,065	18,117
7.	"Black oil"	0.928	86.44	11.83	0.51	1.22	9,977	17,959
8.	A refined oil	(0.904) at 18° C.	85.05	12.15	0.37	2.43	9,998	17,996
9.	A Roumanian crude oil.....	0.825	.....	.....	0.20	....	9,924 (H. assumed 13.0%)	17,863
10.	A Roumanian crude oil.....	0.830	83.77	12.98	0.29	2.96	10,012	18,022
11.	Solar oil (Texas).....	(0.862) at 18° C.	85.35	12.92	0.17	1.56	10,191	18,344
12.	Scottish shale oil.....	0.855 at 18° C.	86.16	12.37	0.26	1.21	10,138	18,248
13.	Scottish shale oil.....	0.862	85.35	12.44	0.29	1.74	10,176	18,317
14.	Scottish shale oil.....	0.867	.....	.....	0.33	....	9,961 (H. assumed 12.5%)	17,930
15.	A coal tar oil (?).....	0.958	86.16	9.05	0.80	3.99	9,422	16,960
16.	A gas oil.....	1.067	87.62	5.98	0.67	5.73	8,974	16,153
17.	A gas oil.....	1.004	83.72	7.29	0.82	8.17	8,876	15,977

sulphur was determined by titration of the bomb liquid, allowance being made for the nitric acid produced in each case. Carbon and hydrogen were determined by the ordinary combustion method of elementary organic analysis.

Open tests were made of flashing and burning points, while viscosity was determined in a special viscometer. The main figures are tabulated in Table I.

Of these oils, Nos. 3, 11 and 14 have been found to work well on Diesel engines, and there is good reason to suppose that Nos. 1, 2, 5, 7, 8, 12, 13 and 14 would work equally well.

Nos. 16 and 17 have been found to give trouble with Diesel engines. As fuel oils probably all the work in ordinary practice. It is astonishing how in ordinary commercial practice the two values are confused. To apply the right correction for the water condensed it is necessary to know the hydrogen in the oil (also the free water if there is any present). To ascertain the correction due to the former cause, the only absolutely reliable means is to determine the hydrogen by making an elementary analysis of the oil. This is, however, a tedious process and in most cases, as will be shown below, the hydrogen content may be assumed with an accuracy sufficient for the purpose of applying this correction in technical work.

In Table II the figures are given for the open flash points, burning points, hydrogen content, gross

calorific value given by the bomb calorimeter determination, the water correction for the hydrogen, the acid correction in the order nitric acid sulphuric acid, and the corrected or net calorific value.

In low boiling fractions of petroleum products, the hydrogen content may reach 16 per cent or more.

At the low temperature end of the curve 0-1 C. makes a very marked difference in the time of flow. This is of imortance when oils are to be used on internal combustion engines. The Diesel engine can take an oil which will not visibly flow at ordinary temperature, if the oil has been subjected to a pre-

TABLE II.

No.	Open Flash Point, ° C.	Burning Point, ° C	Hydrogen.	Cross calorific value (in calories).	Hydrogen Correction	Acid Correction	Net calorific value
1.	133°	164°	11.93	10,644	644	14 (total)	9,906
2.	125°	147°	12.57	10,798	679	15- 7	10,097
3.	125°	155°	(12% assumed)	10,622	(648 assumed)	8-10	9,956
4.	187°	220°	10.81	10,720	584	13- 9	10,114
5.	138°	163°	11.55	10,606	624	13- 8	9,961
6.	166°	197°	11.23	10,690	606	12- 7	10,065
7.	144°	172°	11.83	10,640	639	12-12	9,977
8.	122°	135°	12.15	10,672	656	10- 8	9,998
9.	Ordinary temp.	Ordinary temp.	(13.0% assumed)	10,642	(702assumed)	12- 4	9,924
10.	Ordinary temp.	Ordinary temp.	12.98	10,731	702	11- 6	10,012
11	92°	97°	12.92	10,905	697	13- 4	10,191
12.	129°	158°	12.37	10,825	668	13- 6	10,138
13.	130°	150°	12.44	10,868	672	13- 7	10,176
14.	130°	148°	(12.5% assumed)	10,646	(675 assumed)	3- 7	9,961
15.	77°	106°		9,944	489	9-24	9,422
16.	90°	109°		9,322	324	8-16	8,974
17.	77°	86°		9,295	395	7-18	8,876

It is of interest to calculate the calorific values from the results of analysis and to compare them with those actually obtained by the calorimeter. For this purpose the German modification of the Dulong formula is used, i. e.:

$$81C + 290\frac{O + N}{(H - 8)} + 258 - 6W$$

a formula which gives results, in the case of ordinary coal, within 1 per cent of the actual. It is not meant to be implied that this formula is strictly applicable to oils, but if it is applied, the differences are instructive. Applying this to the oils above, figures are given in Table III.

Figures for fractionation are also appended.

liminary heating. On the other hand, it is possible to have an oil too mobile, which gives trouble by leaking through the valves. If an engine is taking feed at a temperature where the viscosity curve for the particular oil used is steep, trouble will probably be caused by the slight temperature variations making such a marked difference in the rate of flow of the oil.

A curve plotted to show the percentage fractionated at various temperatures shows a steep initial rise in No. 2 and a wave surface with two crests in the cases of Nos. 9 and 10, but the rest do not differ widely from straight lines of varying inclinations to the ordinates.

The tables above bring out in sharp contrast the

TABLE III.

No.	Net Calorific Value.	Calculated Value.	Difference.	Percentage fractionated. 80° C.	120°	160°	200°	240°	280°	320°	360°
1.	9,986	10,300	+344	....	....	....	0	3	15	34	54
2.	10,138	10,529	+391	....	....	6	8	10	20	....	....
4.	10,114	10,315	+201	....	....	....	....	....	0	12	56
5.	9,961	10,295	+334	....	....	....	....	....	14	40	76
6.	10,065	10,193	+128	....	....	....	....	....	6	20	68
7	9,977	10,401	+424	....	....	....	....	4	11	31	....
8	9,998	10,335	+337	....	....	....	....	11	58	....	....
10.	10,012	10,450	+438	6	17	31	41	49	57	....	....
11.	10,191	10,608	+417	....	....	0	11	32	64	....	....
12.	10,138	10,529	+391	....	....	....	....	0	16	70	....
13.	10,176	10,179	—303	....	....	....	0	7	28	....	....
15.	9,422	9,479	+ 57	....	0	4	8	29	....	....	....
16.	8,974	8,639	—335	....	....	....	5	40	55	....	....
17.	8,876	8,620	—256	....	....	(180°) 13		(220°) 86	....	....	....

Curves plotted to show the change of viscocity with temperature show very sudden rises in viscosity at the low temperature end of the curve. For instance, viscosity figures for No. 2 are:

15° C.	18° C.	25° C.	50° C.	75° C.
68-67	31-71	15-57	5-55	2-70

(Water=1.)

distinction between products which have petroleum for their origin and those which have coal. This is especially noticeable in the case of the differences between actual and calculated calorific values which are negative in the latter case.

The two products are entirely different in all their properties, typical mainly of the differences between saturated and cyclic hydrocarbons.

No. 1 fractionated gave the following results:

	Carbon per cent.	Hydrogen. per cent.
1st fraction 13 per cent b. pt. 235-275° C.	84.04	12.16
4th fraction 32 per cent b. pt. above 385° C. (or residue)	87.74	10.45

In the latter case there was some free carbon.

Taking petroleum products by themselves, there is a general relationship between low specific gravity, low flash point, high hydrogen content, low boiling point; but, as is to be expected in such a complex and varying substance, a mixture of many distinct chemical compounds, no absolute relationship can be traced.

THE EVAPORATION OF CHEMICALS.

It has long been known that certain liquids on being evaporated will attack actively the materials of construction of their containers unless some means is developed of limiting this action. The Swenson Evaporator Co. of Chicago, in dealing with this subject, uses many different materials for the construction of evaporators for various purposes, all, of course, being intended for the prevention of corrosion and erosion within the evaporator. Careful study of this subject makes it possible to avoid both repair cost and the annoyance and delay of shutdowns, although in many cases material addition is made to the initial cost of the equipment.

The Swenson Co. makes evaporators for practically every liquid which has to be handled in such a manner: Acid, alkaline or neutral. Not only this, but so careful a study has been made of the action of these various liquids as to overcome the ordinary difficulties in boiling, such as foam and froth, and high boiling point, the precipitation of solids or the viscosity of the liquid treated.

For acids and acid salts the chief difficulties lie in high boiling points and in some cases, the formation of precipitates. The materials used for sulphuric, tartaric, phosphoric acids and acid phosphate are usually lead for the shell and lead or copper for the tubes of the evaporator. For phosphoric acid silver is sometimes substituted as the wearing surface of both shell and tubes. Enamel is frequently used for acid phosphate surfaces. For acetic acid, tannic acid, mixed vegetable acid (whether containing acetic acid or not) copper is the usual construction for both shell and tubes, though bronze is sometimes used for the shell when acetic acid or mixed vegetable acids have to be handled. Tin finds a use in both the shell and the heating surface in some mixed vegetables, while brass or fire clay is sometimes substituted as a shell surface in mixed vegetables containing acetic acid.

The main difficulties in the evaporation of alkalies are the high boiling point to which may be added foaming in the case of soda wood pulp liquors, and foaming and precipitating with carbonate of soda. Cast iron is the common material for evaporator shells in the case of all alkaline liquids, although a lead surface is sometimes used for ammonia and a steel surface for both shell and tubes when carbonate of soda is to be evaporated. Steel tubes or tubes of pure iron are used for practically all these alkalies, copper being sometimes used for caustic potash. The neutral salts, such as sodium chlorides and soap lyes give very little difficulty in operation and are usually concentrated in cast iron evaporators with copper tubes. In many cases of neutral salts steel tubes are used in place of copper, being less expensive and about equally effective. For sugar and stone fruit juices as well as animal liquors, cast iron bodies and copper tubes are used. For vegetable liquors copper is the prevailing element in both body and tubes, although tin tubes are found valuable in some cases.

While the above information is indicative of the general state of the art at the present time, it must be remembered that each case must be considered on its own merits, and in many such cases a deep chemical study of the situation is required to determine what materials should be used.

A syndicate of Chinese has been formed to develop the large and valuable phosphate beds in the Pratas Islands. The islands lie about 170 miles south of Hongkong on the way to Manila. They have long been known to be rich in phosphate deposits, and several years ago a Japanese syndicate was formed for exploiting the deposit on the ground that the islands were no man's land.

At the close of the week ending July 26, 1913, the total output of sugar for the Island of Cuba had been 2,254,232 long tons, according to the semiofficial figures announced. This is in excess of the largest preliminary estimate of the sugar output made at the beginning of the season and is over 350,000 tons greater than any previous production. As on the date given there were 10 mills still grinding, of which 8 were on the north coast, and as the same number of mills last year produced subsequent to July 26 over 50,000 tons, it is probably fair to estimate that the 1913 crop of Cuba will be over 2,300,000 tons.

The mine output of gold, silver, copper, lead, and zinc in California in 1912, according to Charles G. Yale, of the United States Geological Survey, was valued at $26,383,946, an increase of $1,209,260 over the corresponding value for the year 1911. The increase is due mainly to a gain in yield of gold from deep mines, increased value from copper and silver, and increased output of zinc. The greatest gain was in the value of copper and was due to an advance in commercial value of the metal, as the quantity produced was materially less in 1912 than in 1911. To a less degree the same may be said of silver; and the zinc quantities and values also increased.

RAPID AND ACCURATE METHODS FOR DETERMINING PHENOL.*

By L. V. REDMAN AND E. O. RHODES.

In 1871 Landolt[1] made the first successful attempt to determine phenol quantitatively by precipitation as tribromphenol, and since that time numerous attempts have been made to obtain an accurate and easy method of determining phenol each experimenter working under varying conditions to suit his particular purpose. As a result of these investigations, many methods have been submitted for which claims of more or less accuracy and rapidity have been asserted. The time of the reaction period in most cases is too long for rapid determination.

A method has been suggested by Lloyd[2] in which he substitutes a hypobromite solution for Koppeschaar's[3] bromide-bromate solution. In his paper he shows that the tribromphenol is formed almost instantaneously and quantitatively (and that the time of the reaction period is reduced practically to zero). This hypobromite method has been adversely criticized by Oliver,[4] who in 1909 and 1910 published results which do not agree with Lloyd's. He did not find as high a percentage of error when a large excess of hypobromite was added to the phenol as did Lloyd, and he doubts the accuracy of Lloyd's numbers and methods. He shows also that the length of time required for Koppeschaar's method, using a bromide-bromate solution, may be reduced from one-half hour to nine minutes.

More recently, Wilkie[5] has published a method for the rapid determination of phenol, in which he used iodine in cold sodium carbonate solution. The reaction period for this method is 5-10 minutes. It has the disadvantage of requiring that the iodine solution be restandardized each time a phenol determination is made.

A more complete bibliography on phenol determination may be found in Lloyd's[2] paper of 1905 or Wilkie's papers of 1911-1912.

Our object in undertaking this research was to shorten if possible the time required for a determination of phenol by the bromide-bromate method and compare the hypobromite method with the bromide-bromate method for accuracy, ease of manipulation and time required for a determination.

Apparatus.—The apparatus used consisted of a shaking machine driven by a water motor, several five-liter bottles fitted with glass siphons, D. R. burettes and one-half liter ground stoppered bottles from the common stock in which the phenol determinations were made.

The shaking machine is a long, narrow and shallow wooden box 120 cm. × 9 cm. × 9 cm. inside measurements, lined on the inside with felt-covered pads. This box holds twelve one-half-liter bottles. The trough is fitted at one end with a grooved pulley two feet in diameter. At the center of this pulley and also at the center of the box on the end opposite the pulley are steel spindles which fit into the wooden bearings on the supporting frame. The frame is so constructed that this box may be removed and a larger or smaller box substituted. It was possible to rotate the shaker four revolutions per second, but one revolution per second was sufficient.

When a determination was to be made, each of the solutions was run into a 500 c.c. bottle. The stoppers were then placed in the bottles and while being pressed inward were given a short sharp twist. This twist brought the two ground glass surfaces together and made it impossible for any of the solution to leak out or for the stopper to be thrown out when revolved rapidly.

The bottle was inserted between the padded sides of the box. The pressure of the pads held the bottles in firmly. By this construction no clamps are needed to hold the stoppers in the bottles during the time of shaking and the bottles are held in the machine by the pressure of the felt pads, no straps or clamps of any kind being used. This is an advantage, since, by eliminating all clamps, much time and labor, which are important factors when time determinations of small duration are being made, are saved.

In our investigations we made a total of two hundred determinations for which the machine was used and in no case did we experience any trouble or lose a determination on account of bottles flying out or stoppers leaking.

Solutions Used.—The solutions used in the determinations were approximately 0.1*N* solutions of sodium thiosulphate, potassium hypobromite, a mixture of sodium bromide and bromate and phenol, concentrated hydrochloric acid (sp. gr. 1.2), a 20 per cent potassium iodide solution and a starch solution used as an indicator.

The thiosulphate solution was prepared by dissolving 125 grams of sodium thiosulphate ($Na_2S_2O_3.5H_2O$) in five liters of water; 40 grams of liquid bromine dissolved in five liters of *N*/4 potassium hydroxide made up the hypobromite solution and the bromide-bromate solution consisted of 3.5 grains of potassium bromate and 55 grams of KBr per liter. The phenol solution for testing was made from the third distillation at 181-2° C. of Merck's c. p. phenol, 1.46 grams being diluted to 1 liter.

THE HYPOBROMITE METHOD.

In each of the following tables, the order given from left to right is the same order in which the solutions were added for the determinations. The tables show in each case the total volume, the volumes of phenol, hypobromite, hydrochloric acid, potassium iodide and thiosulphate used, and also the time of shaking and

*From the Journal of Industrial and Engineering Chemistry.
[1]Beichte, 4, 770 (1871).
[2]J. Am. Chem. Soc., 27, 16 (1905).
[3]Z. Ann. Chem., 15, 233 (1876).
[4]Rec. Trav. Chim., 28, 362 (1909).
[5]J. Soc. Chem. Ind., 30, 299 (1911).

the percentage of the phenol present which were determined by means of this method.

Table I was prepared in order to determine the effect of time of shaking upon the results obtained, when the total dilution, volume of phenol and volume of hypobromite solution are kept constant and the solution is acid.

The method was as follows: Into a half-liter bottle containing 61 c.c. water the following solutions were added in the order given: Five c.c. of HCl (sp. gr. 1.2), 15 c.c. of 0.1*N* phenol and 19 c.c. of 0.1*N* hypobromite solution. The stopper was then inserted into the bottle and the latter placed in the shaker where it remained revolving for the desired length of time. After shaking, it was removed; 5 c.c. of KI (20 per cent) solution was added to the mixture and the bottle was returned to the shaker, where it revolved for at least three minutes.

TABLE I. HYPOBROMITE.

No.	H_2O.	HCl.	C_6H_5OH.	KOBr.	Time, Min.	KI.	Time, Min.	$Na_2S_2O_3$.	Per cent. Phenol.
1*a*	61	5	15	19	1	5	3	3.99	100.3
1*b*	61	5	15	19	1	5	3	3.98	100.4
2*a*	61	5	15	19	5	5	3	3.97	99.7
2*b*	61	5	15	20	5	5	3	4.98	99.9
3*a*	61	5	15	19	10	5	3	3.88	100.5
3*b*	61	5	15	19	10	5	3	3.97	99.9
4*a*	61	5	15	19	15	5	3	3.89	100.4
4*b*	61	5	15	19	15	5	3	3.90	100.3
5*a*	61	5	15	19	20	5	3	3.91	100.3
5*b*	61	5	15	17	20	5	3	1.90	100.2
6*a*	61	5	15	19	30	5	3	3.88	100.5
7*a*	61	5	15	19	60	5	3	3.86	100.6
7*b*	61	5	15	19	60	5	3	3.91	100.2

Solutions.

Phenol ..... 0.1022 N KI 20 per cent.
KOBr ..... 0.1016 N HCl 1.2 sp. gr.
Thiosulphate ... 0.1003 N

The following table shows the results obtained for one minute to one hour's shaking (the reaction period) before the KI solution was added:

The above results indicate that the time of shaking has very little effect upon the percentages of phenol as determined. It will be noticed that the values for one minute's shaking are as correct as those for one hour. There is no result in the table which varies from the correct value by more than 0.6 of 1 per cent, and the average varies by 0.2 per cent. This is the degree of accuracy claimed by Lloyd for the hypobromite method.

TABLE II.

No.	H_2O.	HCl.	C_6H_5OH.	KOBr.	Time, min.	KI.	Time, min.	$Na_2S_2O_3$.	Per cent.
1*a*	61	5	15	19.0	1	5	3	3.97	100.14
1*b*	61	5	15	19.0	1	5	3	3.97	100.14
2*a*	83.5	5	5	6.5	1	5	3	1.50	99.79
2*b*	83.5	5	5	5.5	1	5	3	1.50	99.79
3*a*	90.4	5	3	3.9	1	5	3	0.92	99.14
3*b*	90.4	5	2	2.6	1	5	3	0.60	99.71
4*a*	92.7	5	1	1.3	1	5	3	0.32	98.90
4*b*	92.7	5	1	1.3	1	5	3	0.31	98.81

Solutions—See Table I.

In Table II are given the results obtained when the concentration of phenol with respect to the total volume was varied but the relative concentrations of phenol and hypobromite were kept constant. In each case the time of shaking was 1 minute and the total dilution 100 c.c.

The results obtained indicate that amounts of phenol as small as 0.000015 gram per cubic centimeter may be determined within 1 per cent by this method and with a reaction period of one minute.

Table III shows that shaking for one minute is sufficient by the method used for an accuracy not greater than four parts per thousand. Each test was run with a total volume of 100 c.c. and in each the concentrations of the various solutions were the same. The six determinations were a single series. All six are submitted, none rejected, thus giving a fair estimate of the amount of the error to be expected generally in a laboratory determination.

Attention is called to the fact that in each of these tables, the phenol was first diluted with water before the hypobromite solution was added to it. *This* is of interest because of the fact that a number of authors state that in the determination of phenol by bromine, a red compound is formed in the white precipitate which is probably tetrabromphenoquinone. Only once or twice in all our determinations did the precipitate show even a light pink shade, never yellow which would indicate tribromphenol bromide, and in all the other cases the precipitate was perfectly white. In every case where the red compound is mentioned the phenol solution was used with greater concentration than $N/100$; it was found that diluting the phenol to approximately $N/100$ reduced the formation of this compound to zero and possibly increased the accuracy of this method.

TABLE III.—HYPOBROMITE.

No.	H_2O.	HCl.	C_6H_5OH.	KOBr.	Time, min.	KI.	Time, min.	$Na_2S_2O_3$.	Per cent.
1	61	5	15	19	1	5	3	3.99	100.3
2	61	5	15	19	1	5	3	3.98	100.4
3	61	5	15	19	1	5	3	4.02	99.6
4	61	5	15	19	1	5	3	4.00	99.8
5	61	5	15	19	1	5	3	4.01	99.7
6	61	5	15	20	1	5	3	4.00	99.8

Solutions—See Table I.

The Permanency of a Hypobromite Solution.—In estimating phenol, conflicting determinations were obtained by us when it was assumed that a fresh hypobromite solution retains a constant quantity of available bromine. Allen[7] states that a hypobromite solution made alkaline by dissolving 62.2 grams of pure NaOH (this is 50 per cent more caustic than is necessary to react with the bromine according to the equation, $Br_2 + 2NaOH = 2NaBrO + H_2O$) and made up to 0.16075 *N* loses not more than 0.8 per cent of

its bromine by boiling it for one hour. Lloyd[7] assumes from Allen's paper that the available bromine in a solution of hypobromite is fairly constant. This is true if the bottle is kept full of solution and corked with a ground stopper. But if the ordinary 5-liter bottle be fitted up with a paraffined bark cork, siphon and inlet for air, the hypobromite solution changes its strength. A fresh solution made up in this laboratory by dissolving 8 grams of bromine per liter in $N/4$KOH changed its strength in thirty-two days from 0.0865 N to 0.0781 N, a decrease of 0.3 per cent strength per day. A second fresh solution of strength of 0.1654 N changed in 12 days to 0.1584 N, that is a change of 0.33 per cent per day. A third solution, which was kept in a ground stoppered brown glass bottle in a dark compartment, changed from 0.1346 N to 0.1340 N in fifty-seven days. It is evident that this solution, which was quite yellow and smelled of free bromine, retained its strength when kept well corked in a brown glass bottle. This may account for the conflicting statements made regarding available bromine in a hypobromite solution. Owing to the possibility of bromine evaporating from a strongly alkaline hypobromite solution it is necessary to test this strength of hypobromite after each determination if these are more than a few hours apart, especially if the solution has an inlet for air to allow the siphon to operate, or if the bottle is badly corked.

TABLE IV.—ALKALINE PHENOL HYPOBROMITE.

No.	H_2O.	C_6H_5OH.	KOBr.	Time.	HCl.	KI.	Time, min.	$Na_2S_2O_3$.	Per cent.
I*a*	64.5	2.5	18	1 min.	5	5	3	19.81	167.84
II*a*	64.5	2.5	18	1 min.	5	5	3	19.78	169.01
I*c*	64.5	2.5	18	5 mins.	5	5	3	19.04	197.25
II*c*	64.5	2.5	18	5 mins.	5	5	3	19.06	196.86
I*d*	64.5	2.5	18	10 mins.	5	5	3	18.96	200.39
II*d*	64.5	2.5	18	10 mins.	5	5	3	18.94	201.17
I*e*	64.5	2.5	18	20 mins.	5	5	3	18.90	202.71
II*e*	64.5	2.5	18	20 mins.	5	5	3	18.89	203.13
I*g*	64.5	2.5	18	1 hr.	5	5	3	18.79	205.49
II*g*	64.5	2.5	18	1 hr.	5	5	3	18.76	208.22
I*i*	64.5	2.5	18	18 hrs.	5	5	3	18.08	234.51
II*i*	64.5	2.5	18	18 hrs.	5	5	3	18.07	234.90

Solutions.

Phenol .....0.1022 N KI 20 per cent
KOBr .....0.1318 N HCl 1.2 sp. gr.
Thiosulphate 0.09816 N
18 cc. 0.1318 N KOBr = 23.72 cc. 0.1 N KOBr
2.5 cc. 0.1022 N phenol = 2.55 cc. 0.1 N phenol

The Acidity of the Phenol Hypobromite Solution.—It is imperative, if hypobromite is used in determining a phenol solution as tribromphenol, to have the solution acid both before and after the hypobromite is added. Otherwise the phenol ring is broken up in alkaline hypobromite and passes over into carbon tetrabromide and possibly higher homologues.

In Table IV the acid was not added until after the hypobromite. Column 5 shows the time during which the solution was alkaline. The table shows the rate at which the bromine is used up in an alkaline phenol solution. The last column gives the per cent of Br disappearing, calculating as 100 per cent the amount of Br required to form tribromphenol, when the solution is acid.

The above table indicates that if the solution be alkaline for only one minute after the hypobromite is added, an error as great as 67 per cent may be introduced in the determination, and a longer period gives a greater error. Lloyd uses sufficient acid to keep this solution strongly acid, although he does not mention the attendant danger if the solution were alkaline. Olivier[10] rather inconsistently expresses surprise at the amount of acid used by Lloyd and at the same time shows that if the solution become alkaline an error of 125 per cent may be introduced in a single determination.

It may be noted that no precipitates appeared after adding the acid.

THE BROMIDE-BROMATE METHOD.

This method is similar in many respects to the hypobromite method. Instead of using a solution of hypobromite as in the first case, a solution consisting of a mixture of potassium bromide and potassium bromate (Koppeschaar's solution) was used. This is the standard solution used by the United States Pharmacopœia and is made as follows: 3.5 grams of potassium bromate and 55 grams of potassium bromide are dissolved in water and then diluted up to 1 liter.

TABLE V.—BROMIDE BROMATE.

No.	H_2O.	HCl.	C_6H_5OH.	Bromide bromate.	Time, min.	KI.	Time, min.	$Na_2S_2O_3$.	Per cent.
1*a*	61	5	15	19	1	5	3	2.80	99.72
1*b*	61	5	15	19	1	5	3	2.75	100.04
2*a*	61	5	15	19	5	5	3	2.80	99.72
2*b*	61	5	15	19	5	5	3	2.77	99.92
3*a*	61	5	15	19	10	5	3	2.80	99.72
3*b*	61	5	15	19	10	5	3	2.79	99.79
4*a*	61	5	15	19	15	5	3	2.78	99.85
4*b*	61	5	15	19	15	5	3	2.77	99.92
5*a*	61	5	15	19	20	5	3	2.73	100.11
5*b*	61	5	15	19	20	5	3	2.80	99.72
5*c*	61	5	15	19	20	5	3	2.75	100.04
5*b*	61	5	15	19	20	5	3	2.82	99.60
6*a*	61	5	15	19	30	5	3	2.70	100.30
6*b*	61	5	15	19	30	5	3	2.74	100.11
7*a*	61	5	15	19	60	5	3	2.70	100.30
7*b*	61	5	15	19	60	5	3	2.71	100.30

Solutions.

Phenol ..... 0.1022 N KI 20 per cent
Bromide bromate 0.09493 N HCl 1.2 sp. gr.
Thiosulphate .... 0.09816 N

This solution has considerable advantage over the hypobromite solution in that it contains no free bromine and therefore does not have the objectionable odor of the hypobromite solution. For the same reason, it is much more stable than this solution[2] and does not require to be standardized with each operation. The chief objection to the use of the bromide-bromate solution, however, has been that it was too slow. Koppeschaar recommends 15 minutes shaking and the U. S. P. 30 minutes, before the KI solution is added.

[7]Beckurts, Arch. Pharm., 5, 24, 561 (1886); from J. Soc. Chem. Ind., 5, 5, 546 (1886).
[8]J. Soc. Chem. Ind., 3, 65 (1884).
[9]J. Am. Chem. Soc., 27, 19 (1905).
[10]Olivier, Rec. Trav. Chim., 29, 294 (1910); Collie, J. Soc. Chem. Ind., p. 264 (1894); Wallach, Ann. Chem., 275, 147 (1893); 159, 322.

As shown by the following tables it is not necessary to shake for one-half hour to obtain an accuracy of three parts per thousand. The order of adding the solutions is shown in each table reading from left to right:

Table V was prepared to determine the effect of time of shaking upon the results obtained when the total dilution, volume of phenol and volume of bromide-bromate are kept constant and the solution acid.

In Table V the constant volumes of water, phenol, acid and bromide-bromate solution were used, but the time of shaking varied. It will be noticed that for no test was there a greater error than 0.6 per cent, and that with one exception all the results are within 0.3 per cent. The results obtained for one minute's shaking are as accurate as those for 15 minutes, 30 minutes and 1 hour.

In order to confirm the one-minute determinations, a series of five tests were run exactly similar to those in Table V. The five results are submitted, none rejected, thereby giving an idea of the magnitude of the errors to be expected in an ordinary laboratory determination by this method.

TABLE VI.—BROMIDE BROMATE.

No.	H_2O.	HCl.	C_6H_5OH.	Bromide bromate.	Time, min.	KI.	Time, min.	$Na_2S_2O_3$.	Per cent.
1	61	5	15	20	1	5	3	5.81	100.4
2	61	5	15	18	1	5	3	3.88	100.4
3	61	5	15	18	1	5	3	3.90	100.5
4	61	5	15	18	1	5	3	3.92	100.3
5	61	5	15	18	1	5	3	3.90	100.2

Solutions.

Phenol ..... 0.08815 N KI 20 per cent
Bromide bromate 0.09493 N HCl 1.2 sp. gr.
Thiosulphate .... 0.09816 N

The results given below in Table VI show an average error of 0.3 per cent, the greatest error being 0.5 per cent for a reaction period of only 1 minute.

Table VII like Table II varies the concentration of phenol with respect to the total volume, but keeps the relative quantity of bromide bromate with respect to the phenol constant. In this table the time of shaking was taken as one-half hour. This length of time was chosen according to the U. S. P., as Table VII was completed before Tables IV and V:

TABLE VII.—BROMIDE BROMATE.

No.	H_2O.	HCl.	C_6H_5OH.	Bromide bromate.	Time, min.	KI.	Time, min.	$Na_2S_2O_3$.	Per cent.
1*a*	61.	5	15	19.	30	5	3	2.70	100.35
1*b*	61.	5	15	19.	30	5	3	2.74	100.11
2*a*	72.	5	10	13.	30	5	3	2.12	100.39
2*b*	72.	5	10	13.	30	5	3	2.15	100.10
3*a*	83.5	5	5	6.5	30	5	3	1.02	101.15
3*b*	83.5	5	5	6.5	30	5	3	1.08	100.00
4*a*	90.4	5	2	2.6	30	5	3	0.39	102.92
4*b*	90.4	5	2	2.6	30	5	3	0.43	100.05
5*a*	92.7	5	1	1.3	30	5	3	0.19	102.50
5*b*	92.7	5	1	1.3	30	5	3	0.21	100.58

Solutions—See Table V.

The results for 1 and 2 c.c. of phenol are seen to be less concordant than those for larger amounts. However, as one drop is an error of 5 per cent in 1 c.c., and as the phenol solution was measured out from a burette and not weighed, the agreement is fairly good. The table shows that 0.000015 gram of phenol per cubic centimeter may be determined by this method with a maximum error of 2 per cent. The method is probably much more sensitive than this if more dilute solutions are used.

From these tables we have come to the following conclusions for work requiring an accuracy not closer than 0.3 per cent. *First*, it is not necessary to shake the acidified phenol solution with Koppeschaar's solution (bromide bromate) or with Lloyd's hypobromite solution for a longer time than one minute if a continuous shaker is used. *Second*, if the conditions of dilution, etc., are those given in the preceding tables no red or yellow compounds are observed in the white tribromphenol precipitate.

In addition to the above experiments, tests were run by the two methods to determine the error which might be introduced in the determinations due to chemicals, evaporation of bromine due to the use of ordinary one-half liter bottles, methods of working, etc. Thus, an error might be introduced by running the hypobromite solution into the phenol without shaking if the region where the hypobromite was most concentrated became alkaline. Several tests were made to determine this, but no appreciable effect was noticed.

A series of six determinations to find the effect of titrating back with the thiosulphate after periods of 1, 2 and 3 minutes (continuous shaking) from the time when the KI was added, gave results which showed a maximum error of 0.5 per cent within themselves. Accordingly an error of not more than 0.5 per cent. is introduced if the solution is shaken only 1 minute after adding the potassium iodide.

Blank experiments were run under the same conditions as the original determinations which showed that the maximum error introduced by the solutions, manipulation, bottles, etc., was 0.3 per cent.

Directions.—(1) N/10 sodium thiosulphate and a N/10 of either hypobromite or bromide bromate, 20 per cent KI and ½ per cent starch solutions.

(2) Into a 500 c.c. bottle, fitted with a ground glass stopper, put 60 c.c. water, 5 c.c. hydrochloric acid (sp. gr. 1.2) and then add 15 c.c. of the unknown phenol solution which is to be determined and which has previously been diluted to about N/10. If the solution is weaker than N/10 no previous dilution is required. Add quickly enough N/10 hypobromite or bromide-bromate solution to make the solution yellow and then add in addition 10 per cent of the amount already added. Place the stopper in the bottle and shake continuously for one minute. Add to the solution in the bottle 5 c.c. potassium iodide solution (10 per cent) and again shake for three minutes. Wash down the stopper and sides of the bottle and titrate the solution

with the $N/10$ thiosulphate, using starch solution as an indicator. The starch must not be added until enough thiosulphate has been run in to make the solution almost colorless. The quantity of thiosulphate used represents the quantity of free iodine, and therefore the quantity of excess bromine. The difference between this quantity and the known quantity of bromine added gives the amount of solution present. Each cubic centimeter of $N/10$ bromine used up is equivalent to 0.00156 gram of phenol.

SUMMARY.

I. The results show that by the above methods of manipulation, either with the hypobromite or with the bromide-bromate solution, phenol determinations can be made within an error of 0.3 per cent with only one minute of continuous shaking after the solution containing the bromine is added, *i. e.*, the reaction period may be reduced from 30 minutes to 1 minute without sacrificing accuracy.

II. The phenol in each case was diluted until it was approximately $N/100$ before the determination was made. The resulting precipitate with the hypobromite or bromide-bromate solution was white and flocculent in each case and the precipitate showed no traces of red tetrabromphenoquinone or yellow tribromphenol bromide.

III. In order to secure correct results, the phenol solution must be acid after the bromine is added. If it is alkaline, an error is introduced which increases as the concentration of the phenol in the solution diminishes and the reaction period increases.

IV. The error introduced by shaking the solution for only one minute after the KI solution is added before titrating back with thiosulphate is 0.5 per cent. Three minutes shaking eliminates this error and longer shaking has no effect.

V. The bromide-bromate solution has the advantage over the hypobromite of being permanent. When the solution used was first made, its strength was 0.09493 N. After three months duplicate tests gave 0.09495 N. The hypobromite solution weakened one-third per cent every twenty-four hours for the first few days after the solution was made. The bromide-bromate solution has not the unpleasant odor of free bromine.

ALASKA METAL PRODUCTION.

The United States Geological Survey has just issued, as an advance chapter from "Mineral Resources of the United States," a report by Alfred H. Brooks on the mine production of precious and semiprecious metals in Alaska in 1912. Metalliferous mining in Alaska, says Mr. Brooks, made important advances last year. Although the output of gold placers was less than in 1911, the installation of large plants, notably of dredges, in many districts is encouraging for the future of this industry. More important was the progress made in lode gold mining, the output of which was greater than in previous years. Copper mining also advanced, partly because several large plants increased their output, partly because a number of small mines were developed on account of the high price of copper.

The development of the coal fields still awaits the establishment of a definite policy in regard to the disposition of the public coal lands. The delay in securing cheap fuel for the Territory has now for many years caused a stagnation in many industries. Railway construction and, to a certain extent, railway operation have stopped and many mining enterprises have been hampered if not entirely abandoned on account of the uncertainty as to the fuel problem. Very few Alaskans have any direct interest in coal claims or in mining, but the entire population of the Territory is desirous of seeing the coal fields developed, because it is believed that this will bring about advancement in many other industries. Above all, it will encourage the operation and the construction of railways, which are all important to the Territory.

The total mine production of gold, silver and copper in Alaska in 1912 was valued at $22,285,821, against $20,505,664 in 1911, an increase of $1,780,158. The value of the gold production of Alaska last year is estimated at $17,145,951, that of silver at $316,839. In 1911 the output of gold was valued at $16,853,256. The copper output of Alaska for 1912 was 29,230,491 lbs., valued at $4,823,031, an increase from 1911 of 1,962,613 lbs.

According to the June issue of the *Indian Textile Journal*, the conversion from steam to electric drive of cotton mills and other factories by the Tata Hydroelectric Co. will shortly be taken in hand. The contract for this important work has been entrusted to the British Westinghouse Co. The motors will all be of the Westinghouse "AIF" slipspring protected type, suitable for double drive, and for 3-phase current, at 2,000 volts and 50 periods. At present a total of 207 motors of this type have been ordered, the sizes ranging from 50 to 500 brake horsepower. The motor speeds are 290 and 365 revolutions per minute, there being several of each horsepower capacity at these speeds. With regard to the drive, the motors will be coupled direct to the

---

Slate and shale are used to a considerable extent in the manufacture of pigments and as fillers in the manufacture of oilcloth and linoleums, the total quantity used for this purpose in 1912, according to the United States Geological Survey, being 20,964 short tons, valued at $121,482. This was an increase of 4,454 tons in quantity and of $16,031 in value over the output for 1911. The 1912 output of slate and shale used for paints and for fillers came from Pennsylvania, New York, New Jersey, Indiana, California, and Georgia—named in the order of their production, Pennsylvania producing over 84 per cent of the total output in the United States.

Gasoline exports from the United States in the fiscal year 1913 amounted to 82,000,000 gals.

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What's the Matter With the American Chemist.

The Journal of Industrial and Engineering Chemistry has recently published three articles under the heading "What's the Matter With the American Chemist?" We are republishing these articles as we believe they present some facts which ought to be regarded by our American chemists and our American chemical manufacturers.

I.

By DANIEL M. GROSH.

A recent news item in the daily journals should furnish food for some very serious reflections. In brief, it stated that the American textile manufacturers have for years been under the domination of the foreign dye trust and are at last beginning to revolt. Why this industry is so dominated, why they have not revolted heretofore, and what their revolution will bring forth are well understood by any person who has studied the subject and is familiar with the status of commercial chemistry in America.

The industry mentioned is forced to use large quantities of imported dyes because they are superior to most of the domestic dyes and are also forced to pay $1.00 per pound for a product for which they formerly paid 25 cents.

What's the matter with the American chemists that they cannot supply their own market? Is it possible that they cannot, with all their vaunted genius and mechanical ingenuity, and with the protective barrier of a high tariff, exclude these as well as other articles of foreign manufacture?

To acknowledge we cannot make as good products as foreign chemists is not only humilating but true, not only in the chemical industry but in others also and the reason for it is that the foreign producer has worked on the basis of making the best goods at the lowest cost and makes them under the intelligent supervision of modern science.

American chemists individually are just as brilliant, well educated, energetic and ambitious, hence the cause is elsewhere. Our educational institutions are surely competent and possess the necessary facilities, so where does the difficulty lie? Simply in the fact that science has been relegated to the rear and that the American chemists do not get the encouragement and co-operation needed to develop their activities sufficiently to meet commercial requirements.

Our manufacturers have been concerned primarily in producing goods to make money and have always had every advantage in their favor. A large demand due to an increasing population, plentiful and cheap raw material and fuel, efficient machinery and mechanical appliances, shrewd financial management and business combinations and again the highly protective and benevolent tariff. We have never felt the heavy hand of competition as have English and European producers and yet with every advantage we cannot produce first-class goods.

Germany's encouragement of the chemist, both financial and educational, and the application of scientific methods to industrial needs in general and chemical productions in particular their eagerness to utilize any new knowledge in their factory operations, and most of all a willingness to spend money in experimenting and developing ideas and processes, are the reasons why that nation to-day is gradually absorbing the commerce and business of other nations. France long ago realized her danger and is rapidly applying science to industrial ends and even Italy, a nation of supposed lethargic temperament, is keeping in the front rank.

England has already felt with much concern the iron hand of the Teuton reaching out over the seas and gathering in the business of the world and our turn will be next. No less authority than Prof. Perkin recently stated that these are indeed parlous times, and England's commercial future depends upon scientific industrial chemistry and to that alone the nation must turn.

It is no exaggeration to say that the situation in America at the present time is chaotic. The complaint of the textile industry is characteristic and confirms this assertion in their single charge that they cannot get domestic dyes of quality and are being plucked for what they are forced to import.

The American producer is laboring under the impression that when he attains mechanical perfection

in his factory he has all that is to be had. Mechanical contrivances are well and good, but they are only a small part of modern industrial operation. Nearly all operations are dependent upon raw material; raw material is substance and that in its turn is chemistry and every industry or process involved is to that extent chemical; wherever we turn this fact stands out most prominent.

From the very nature of things, education to-day is largely a matter of books, and while much valuable information and training are obtained from this source, there is one vital element to success, not only in chemistry but in other professions, which is often neglected. This element is called common sense but experience shows that it is indeed far from being common.

In solving the industrial problem of to-day its intelligent application is equally as important as professional knowledge. It is no more possible to solve a chemical operation of magnitude by abstract principles than it is to diagnose a disease, repair a mangled machine or conduct a legal case.

In no other country but Germany does there exist such co-ordination and co-operation between the industries, institutions of learning and finance. A typical instance may be given in the discovery, by a German teacher, of a new process. His first effort was to present it to the expert of a great factory concerned in its production, then to the great financial institution of Germany, the Deutsche Bank. As a result, the factory with its producing facilities, the bank with its backing and financial aid, and the discoverer with his process form a company of three.

Imagine the reception a chemist approaching a bank in this country would get! Nothing is harder to get in this country than financial assistance to develop a chemical process. Many individuals have the idea that chemistry is merely a routine operation, and it is no secret that a chemist in developing an industrial process has his own troubles. Numerous instances can be given where the establishment of a factory laboratory would save thousands of dollars to the producer, but he apparently prefers jogging along in the "save at the spigot, lose at the bung" gait of his forefathers.

Any process to be of industrial value must be perfected on industrial lines and while a laboratory reaction will give all that may be desired, the same reaction with tons of material to work with instead of grams, means something different, as many have discovered to their confusion and sorrow. Many operations successful in the laboratory have been a failure when conducted on a large scale and the chemist condemned along with his process when the fault could have been avoided by an intelligent application on a different basis.

Chardonnet made a dead failure of his artificial silk process when he tried it out commercially, not once but four times, but financial assistance was given him, instead of condemning him as a fraud or fakir, and the process as a swindle. German chemical firms spent millions before a dollar's worth of goods was marketed. The chances are that an industrial chemist in this country who could not revolutionize conditions or produce ideal results in a few months' time would be fired for not knowing his business.

So much stress has been placed upon the value of chemistry in the industries of to-day that the majority of people have the most vivid ideas concerning it. They do not know that each application of its benefits meant perhaps years of persistent and unpaid toil. An individual once came to the writer to perfect a certain process which would ultimately devolve into a business of enormous proportions. When informed that a sum of money would be required for a special laboratory, trained workers, equipment and material, it almost produced apoplexy. He was ready to benefit but would not pay research expenses, had no idea chemistry involved such work, required such time, etc.

Certain conditions exist in the commercial world of industrial chemistry that are inexplainable and almost ludicrous. Why do we import essential oils to the value of millions each year when we have all conditions, climatic and otherwise, for their domestic production? Why is impure bauxite imported by shiploads when we have aluminous ores, rich in alumina, free from iron and calcium by the millions of tons in our own land? Why do we use the chemical process for producing the enormous quantity of alum consumed, when from the same source pure sulphate alumina can be loaded on cars like sand from a sandbank?

No wonder foreigners say we are insensible to and unappreciative of the good things nature has provided. No fault can be found with the American chemist individually, but the system or promoting and developing the chemical industries and applying science to commercial requirements, needs a severe and an awakening jolt unless we want to be brought to our commercial knees.

5927 Walton avenue, Philadelphia, Pa.

II.

Editor of the Journal of Industrial and Engineering Chemistry:

I feel the need of expressing myself on some of the ideas put forth in the address of Mr. Daniel M. Grosh in this journal, 5, 692.

Years ago I was engaged with other chemists in promoting the development of the American dyestuff industry, by sitting comfortably in the laboratory and lamenting its comparative insignificance. In the midst of our lamentations the boss walked in and started things by remarking, "Quit your tin-canning and get to work."

What is the use in celebrating the ability, the energy and efficiency of the American chemist and damning the manufacturer and capitalist?

The manufacturer and capitalist won't be convinced of the error of their ways, and their lost opportunities for fortune, by talk or printers' ink. They must be shown and they won't need any more showing than their German analogues, though, of course, Rene Bohn, for instance, will have less trouble in showing a German than John Smith, A. C., will have in showing an American.

John Smith, A. C., is up against certain conditions that he must meet, and "tin-canning" isn't the best method of approach. If John Smith, A. C., has a job and will adapt himself to American manufacturing conditions, he can make good if he has anything to make good on. But if he is infected with *B. research tersanctus*—God help him.

Cords of good white paper and millions of cubic feet of air are used up annually in extolling research but the average young chemist doesn't know what the word means. As nearly as I can judge, he thinks it means from $1,500 to $2,000 a year, a beautiful white laboratory, and plenty of time in which to read the morning paper and wait for inspiration. If he will realize that commercial research means a dollar sign and not a halo, and go to work on the problems that present themselves with the means at his disposal, or that can be obtained by the exercise of all his tact, he may know what research means after a year or two.

As the American dyestuff industry is generally taken as the "horrible example" in these lamentations, I hope to be allowed to state that a large number of useful dyes are made in this country and they are just as good as the same dyes of German make.

Furthermore, if John Smith, A. C., has any well-developed plan by which the American Coal Tar Color industry can be extended, I know where he can find all kinds of financial support for it. It should be understood, however, that while Rene Bohn can probably get backing for a test tube experiment, John Smith, A. C., will have to show something more.

W. H. Watkins.

III.

Editor of the Journal of Industrial and Engineering Chemistry:

In Mr. J. M. Matthews' reply to Mr. Grosh's article with the above title (this Journal, 5, 626 and 692, respectively), he states that one of the main troubles with the American Chemist is that he wants real money for his service, truly a heinous condition, while his German colleague is willing to work on "prospects." We have heard the dogma preached from Wall street for many years: "Young man, don't work for money. Work for experience and when you are old enough we will give you a nice little pension."

The trouble is not with the chemist but with the manufacturer. Instead of regarding his research chemist as a highly trained specialist, he regards him as a day laborer, makes him punch a time clock and thinks that if favorable results are not obtained immediately, the man is not worth his hire. Would he for one minute think of putting his physician on such a basis—*No Cure, No Pay?*

In the case of the physician or lawyer, even laymen can appreciate the difficulties with which he struggles, but the chemist battles only with "the innate perversity of inanimate things," and that, as we all know, is absurdly easy!

Of course, the manufacturer has had enough experience with "has-been," "would-be" and "analytical" chemists who pretended to be "research" chemists. It is this class who have puttered away the manufacturer's time, money and patience and prejudiced him against research. These "has-been" chemists, too, are always crying that there is a vast difference between laboratory and factory research.

There is only one kind of research, and that is research that brings results to the person who commands it. The skilled research chemist must have a large modicum of "horse-sense" which is acquired neither by experience nor association.

And after all, suppose a young chemist has worked for some time on "prospects" and finally has achieved something for a manufacturer. What guarantee has he that his work will be remunerated? Will there not be hundreds of new chemists waiting eagerly in the bread line for some manufacturer to let them work on prospects?

In a great many cases, having obtained the best products of a man's brain, there would be no further inducement for retaining him. Sidney Born.

Decreased Borate Ore Production.

According to an advance chapter from Mineral Resources on the production of borax in 1912, by Charles G. Yale and Hoyt S. Gale, just published by the United States Geological Survey, there was a decrease in the production of borate ores in the United States last year. The output of borate ores in 1912 was 42,315 short tons, valued at $1,127,813, as compared with 53,330 tons in 1911, valued at $1,569,151. The quantity stated is that of the crude ore as mined for delivery at the mill or for shipment.

All the borax now produced in this country is derived from ores mined in California; in fact, virtually the entire product is derived from four mines—one in Inyo county, one in Los Angeles county and two in Ventura county. Formerly borax was obtained from the so-called marsh or dry lake deposits, which were worked in Nevada, California and Oregon. The borax and boric acid now produced is derived wholly from deposits of borate of lime, in which colemanite is the entire source of supply.

There is a general impression that colemanite has been found in so many places and in quantities so large in relation to the small demand for borax and boric acid in the present market that there need be no fear of the exhaustion of the deposits. In fact, however, in nearly all deposits mining had proceeded

with great rapidity and possibly in a more or less wasteful way. Mining entries are generally driven ahead somewhat at random, the pockets of ore being "gutted" and shipped before attention is directed to the blocking out of ore in reserve. If this practice is continued even the large deposits of colemanite now known will not last indefinitely, and the exhaustion of one after another of the workable deposits is expected. Since the discovery of colemanite in 1882 at least one large district has been worked out and abandoned.

Even should the richer deposits ultimately become exhausted, however, there are many other possible sources of supply, including the marsh deposits formerly worked, to which recourse could again be had. More important than this, a new factor is entering the field of the borax industry with very recent developments. The natural saline deposits of the Western desert region have come into prominence as a possible source of potash, carbonate of soda, common salt and other products, including borax, as one of the very promising marketable by-products of any industry that may succeed in developing the other salts in a commercial way.

Working Salmon Offal.

Salmon offal yields 10 per cent of oil and 25 per cent of fertilizer material. This material cannot be worked by the same methods as are used in the menhaden industry. If the fish are thoroughly cooked the entire mass will be forced through the press. If the fish are undercooked the oil cannot be thoroughly removed. In order to produce a fertilizer material of high quality it is absolutely essential that a high percentage of the oil be removed. Extraction by means of solvents such as benzine, benzol, is not at present practiced, but there seems to be no reason why it cannot be done as cheaply and more thoroughly than by pressing. It must be understood that the action of steam alone will not render the scrap ready for the presses. Something must be added to prevent the material from gathering gases and becoming spongy. Every producer uses his own method, which is kept secret. This is the most difficult part of the process, and is the stumbling block of manufacturers who are inexperienced.

A bill has been introduced in the House of Representatives, H. R. 7152, by Representative Doremus, of Michigan, a member of the Interstate and Foreign Commerce Committee, to authorize and empower the Public Health Service to collect, maintain and make available plans and descriptive matter relative to hospitals, asylums, dispensaries, etc.

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UTILIZING WOOD WASTE.*

By JOHN E. TEEPLE.

I have been asked to give a general survey of the field of chemical wood waste utilization: what has been accomplished, what is being done, what are the prospects. In such an address many interesting details must be omitted, many subjects passed over lightly or merely mentioned; much of the material presented will be familiar to many of you, and a part to all of you.

Man has been utilizing wood from the beginning. Wherever we find him in history, even as a barbarian, he has known how to make charcoal and probably tar from wood, if he had the wood; and there was abundance of wood. Central and Northern Europe were almost entirely forest or swamp. The larger part of our own country, excluding the middle western prairies, was covered with trees. Nearly this whole state of New York, this spot on which we stand tonight, was a forest. There was no waste wood, or it was all waste, just as you choose to consider it. The whole forest was a huge storehouse from which man drew indiscriminately whatever was best suited or most accessible for timber, for lumber, for charcoal, for tar. The settlers cleared millions of acres for agriculture by simply chopping down the trees and burning them where they lay.

It has remained for our own time, our own generation, the last few years in fact, to develop a problem of wood waste utilization and to make some progress toward its solution in a chemical way. In our day, ideas of conservation are prevalent and directing. The tar or charcoal burner of two or three hundred years ago in Russia or Sweden, and more recently in the Carolinas, centered his interest in the tar for his ropes or the charcoal for gunpowder or metallurgical purposes. Today we approach the same manufacture with a view to utilizing waste materials. Here are certain residues unsuited for lumber, lath, railroad ties or box shooks, good only for fuel and unsalable at fair prices as fuel. What shall we do with them? Shall we or can we make tar or rosin, or alcohol or paper, or anything else that is marketable, and can we also secure a profit in doing so? The profit side is important because no matter how remarkable transformations are accomplished, or how interesting the process may be from a chemist's view point, still the law holds: no profit, no industry.

In this discussion we shall restrict ourselves mainly to this continent, mentioning only incidentally the work in Russia, Sweden, Austria Hungary and other European countries. Our subject of wood waste naturally excludes most of the manufacture of paper pulp from spruce, poplar and hemlock, and some of the hardwood distillation, the extraction of tanning materials, dyestuffs, etc. In these excluded cases we are not specifically utilizing waste materials, but are competing for the purchase of raw materials which are in some demand for other industries.

RAW MATERIALS.

A list of the important woods of this continent, which from their use for lumber would be a source of wood waste, would extend to more than a hundred names. For our purpose we may classify such as are of present interest as follows: First, the longleaf pine (*Pinus palustris*) in all the states touching the Atlantic Ocean or the Gulf of Mexico from North Carolina to Eastern Texas. This wood is exceedingly rich in resins and terpenes, and this tree makes the United States the largest producer of turpentine and rosin in the world. Second, the shortleaf pine (*Pinus echinata*) of the same distribution but extending farther inland, especially in Arkansas and Missouri, contains comparatively a small amount of resins and terpenes. The loblolly (*Pinus taeda*) and the Cuban pine (*Pinus Cubensis*) are intermediate between these two in their characteristics. These are the most important Southern pines. In the North, the Norway pine (*Pinus resinosa*) occurs in Minnesota, Wisconsin, Michigan and the Province of Ontario. It does not occur in forests, but is scattered among other timber and in groves. A large portion of this has already been cut, and the waste for our purpose is in the form of stumps on uncleared lands. Like the longleaf pine and other resinous trees, these stumps do not rot. The bark soon falls away, the layer of sap wood decays, but the remainder apparently becomes more resinous with the years.

On the Pacific coast the Douglas fir (*Pseudotsuga Douglasii*) is especially abundant in British Columbia,

*Paper presented before the New York Section of the Society of Chemical Industry, Chemists' Club, April 25, 1913.

Washington and Oregon. Individual trees vary considerably in character; some are rich in resins, particularly where it has collected in pockets or wind shakes; others contain very little. The amount being cut by lumber mills is very large, and any method of utilizing the waste either from mills or from stumps must recognize the variation and select the material suited for its purpose.

We next have the class of wood suitable for what is called hardwood distillation and including white pine, maple, oak, beech, birch, chestnut, ash and some other broad-leaved woods. These are the chief types having marked characteristics that have led to especial efforts for utilizing their waste.

Considering next the form of waste, the most immediate one is lumber mill refuse. It consists of sawdust, the slabs, edgings and ends of the lumber. The sawdust and ends will have about the same average composition as the logs, but slabs and edging contain a larger percentage of bark and sapwood. All the refuse is of course green and contains twenty-five to fifty per cent moisture. When cutting longleaf pine that has been boxed for turpentine, many of the slabs are very resinous. Second, the limbs and tops left in the woods by lumbering operations; some of this can be gathered for hardwood distillation, but with the amount of other waste more available, the greater portion remains in the woods and soon decays or is burned. Third, the stumps; in resinous conifers these are the richest and most valuable for recovery of turpentine and rosin. Other stumps are too irregular and too expensive to utilize at present. A fourth form is the resinous "lightwood" from longleaf pine trees which have died standing or have been blown down by winds. This has heretofore furnished a chief part of the coniferous woods used for distillation.

COMPONENTS OF WOOD WASTE.

Disregarding the bark, we may consider all trees as composed of cells and ducts or interstices through which the sap flows. These cells are added in rings or layers externally, one ring for each year; a light colored part representing the spring growth and a darker colored part the summer growth. In conifers the colors are so sharply defined as to present two distinct rings, the summer growth here containing much more resin than the spring growth, and the percentage of summer wood decreases regularly from stump to top. In young trees the cells consist entirely of cellulose; in age they become encrusted with lignin or a ligno-cellulose ester. The sap is largely water. Green wood contains twenty-five to fifty per cent water, air-dried wood about twenty per cent, and wood dried at 150° carefully may be entirely freed of water. Such dried wood contains about 1 per cent mineral matter and the remaining cellulose and lignin contain about fifty per cent carbon, six per cent hydrogen and forty-four per cent oxygen. In addition, resinous conifers contain oleoresins, differing somewhat in each species. These are apparently simple mixtures of resin acids (rosin), volatile terpenes (turpentine), and in the case of lightwood, various higher boiling terpenes, terpene alcohols and esters (pine oil), probably formed from the terpenes by hydrolysis and oxidation. These pine oils occur in small quantities in green wood, but do not appear to any extent in the gum flowing from longleaf pine trees when they are chipped for turpentine.

Water, cellulose, lignin and the oleoresin which contains rosin, the terpenes and terpene derivatives are the only constituents of any class of wood waste so far as we are concerned. Any other product derived from wood waste can come only by chemical transformation or decomposition of these constituents.

THE PRIMARY MARKETABLE PRODUCTS.

Paper Pulp.—We have mentioned cellulose, or at least the cellulose part of the lignocellulose complex, as one component of wood waste. By removing the other constituents we can obtain cellulose, and wood waste then can be an important source of paper pulp. Hitherto it has not been. The raw materials for both chemical pulp and mechanical pulp or wood flour usually have been carefully selected and are comparatively high in price. This high price has caused diligent and successful search for other raw materials. Sapwoods of shortleaf and loblolly pines were commercially added to the list of pulp woods. The investigations, naturally extended to wood wastes, showed that most of them from Southern pines at least were capable of yielding merchantable paper pulp under proper treatment by the soda or sulfate methods. The sulfite method is said to be less satisfactory.

It has still to be demonstrated whether the number of plants now projected will repeat in a commercial way the success that has attended the laboratory experiments in a chemical way. It is doubtless true that nearly any laboratory success or result that indicates financial profits can be repeated commercially; but the development of a laboratory process into a working plant paying dividends is a much harder task than is often realized, and many times requires years of united effort on the part of the best chemists, engineers, chemical engineers and business managers before it is accomplished. In this specific case, at least one plant has made pulp from waste wood, and transformed the pulp into very good grades of wrapping paper that have found a market. We are discussing the state of an industry and this one example brings paper pulp into our province. The advantages of waste wood for paper pulp are its cheapness and its quantity. The disadvantages are several. If made from mill waste the wood is green, full of water, has a large percentage of bark, and comes in irregular shapes. This means poor quality of pulp or large labor cost in selecting and greater manufacturing cost. If dead or fallen timber is used in conjunction with turpentine and rosin extraction by solvents, it will contain a large proportion of knots and charred wood unless

carefully separated by hand. Shavings from a planing mill are comparatively free from all these disadvantages, and this has been used with success.

Ethyl Alcohol.—Since wood waste contains cellulose, it must be regarded as a source of ethyl alcohol. The raw material used is bulky compared with the finished product and must be cheap in initial cost and have no labor charge for preparation or handling. This has so far restricted it to unselected mill waste from large lumber mills. Hydrolysis of the cellulose with very dilute acid produces glucose and fermentation of the glucose and distillation of the resulting mash gives a very satisfactory grade of ethyl alcohol. Some of the patents are over twenty years old. An unsuccessful plant was established in Mississippi nearly ten years ago. The processes are beautifully simple on paper, and in the laboratory, but it is only now that we can begin to say we have such a manufacture commercially. Years of experiment have been spent in determining the most favorable conditions of hydrolysis. The kind of acid, sulfuric, sulfurous, or hydrochloric, the per cent strength of acid and proportion to wood, the amount of water, the temperature, pressure, time, have all been found important factors in hydrolysis to obtain the maximum yield of fermentable sugars, and the minimum loss of those sugars by decomposition. Then problems of proper neutralization of the saccharine liquors and removal of extracted materials that prevent or retard fermentation; the development of special yeasts and the fermentation methods for the liquors; the treatment of residues to furnish suitable fuel for the plant. All these problems have now received solutions adequate enough to furnish a total production of 5,000 to 10,000 gallons ethyl alcohol per day from wood waste in two plants, one in South Carolina and one in Louisiana, both working on mill waste from Southern pines. The field is an interesting one, and in view of its possibilities should be attractive to investigators.

Acetate of Lime, Wood Alcohol and Charcoal.—When wood is heated somewhat above 200° decomposition begins. Water distils first, then dilute acids, mainly acetic. At about 275° considerable wood alcohol is in the distillate, and light tar oils and gas are flowing freely; at a higher temperature heavy tar oil flows, and finally only charcoal is left in the retort. With uniform and careful heating 350° produces good charcoal and 300° brown charcoal, although observed temperatures on retorts are usually higher owing to unsatisfactory heat distribution and transmission. The reaction is exothermic and above 280°, with proper insulation, will support itself. Cellulose distilled alone gives no methyl alcohol, but otherwise the phenomena are the same. We must look to the lignin part of the wood for the methoxy groups furnishing methyl alcohol. No matter what wood is distilled there will be the same products, varying, however, in quantity with the kind and dryness of wood and with the rapidity of heating or speed of removing products from the retort during distillation.

The manufacture of acetate of lime, wood alcohol and charcoal has not been essentially a wood waste utilization industry. Individual plants often take a part of their wood in the form of slabs from adjacent hardwood sawmills; one small plant recently started operating in Tennessee on oak slabs, but commercial figures are not yet available. In the main, plants have been established not primarily to use waste material, but to supply a demand for charcoal in nearby blast furnaces. Slabs are of course cheaper than cordwood, but the yields obtained from them are somewhat smaller, and a belief has existed in many quarters that they could not be satisfactorily distilled alone. The yields from good air-dried hardwood are of charcoal 30 per cent, or a little less, wood alcohol 10 gallons per cord, 82 per cent gray acetate of lime 200 lbs. Pine woods give much smaller yields, the type usually distilled in the South, for example, producing only about 20 per cent charcoal, one to two gallons methyl alcohol per cord, and 50 to 75 pounds acetate of lime, either brown or much more difficult to refine than the product from hardwood. Recovery of these smaller amounts of alcohol and acetate has been attempted in a commercial way, but is now entirely abandoned. Charcoal from pine wood usually commands a ready sale for household or manufacturing fuel, if the plant is favorably located.

Turpentine, Pine Oil and Rosin.—Coniferous woods in general, and the longleaf pine, Norway pine and Douglas fir in particular, contain oleoresins. These are partly physiological and mainly pathological secretions of the resin ducts, and are not to be confounded with the sap of the tree. When a coniferous tree is wounded a secretion flows from the wound. In the case of the longleaf pine, the wound must be reopened by chipping at least every week to keep the gum flowing. Since the oleoresin is so largely a pathological product, the more the tree is wounded and the larger amount of oleoresins we take from it in this manner, the more remains or is formed in the body of the tree, and the richer we find it when we work it up as waste wood. This oleoresin may be completely separated by chipping the wood and extracting thoroughly with a solvent. Fractional distillation of the extract, usually in the presence of steam, separates it into solvent, turpentine, pine oil and rosin. These are the only products directly obtainable from the oleoresin, and none of these is obtainable from any other portion of the wood excepting the oleoresin. Of course, it is not necessary to isolate the oleoresin. Direct heating of the wood will drive off the turpentine and pine oil, and if the heating is continued will melt out part of the rosin, decompose the rest of it, and mix rosin naphtha or rosin spirit with the turpentine.

Simple steam distillation of the wood will remove most of the turpentine and pine oil alone. However these products are extracted, they will be slightly different from the turpentine and rosin obtained by chipping the tree. The turpentine is liable to be contaminated with the products of distillation of the rosin,

or of the wood, or of the bath, or of the solvent used in its preparation. If considerable heat or pressure has been used, particularly in the presence of acids either already in the wood or derived from its decomposition, partial transformation of the pinene to dipentene occurs. Methods of refining have now progressed so far, however, that, where proper care is used in manufacture, a very satisfactory and uniform turpentine is marketed. It has a slightly different odor from gum turpentine, and even the best of it in a commercial way does not quite meet the specifications as to the amount distilling between certain limits, as does gum turpentine. This is apparently due to a slightly larger content of dipentene or *B*-pinene or both. This difference in proportion of constituents makes a slight difference in its solvent power. When properly made and refined, it finds widely extended use wherever gum turpentine can be used. So far as I know it contains no constituents that are not present in ordinary gum spirit of turpentine.

The rosin extracted from wood has usually been of about an E grade, so far as color is concerned, but has been somewhat softer than the corresponding grades of gum rosin. This is due to a certain amount of heavy oils, about one per cent, which still remains in the rosin extracted from wood. This remaining one per cent of oil can be removed under proper conditions, and when this is done the rosin extracted from wood is not in any respect commercially different from the gum rosin. Most of the plants up to the present, however, have not removed this last fraction of heavy oil, and have been content to market their rosin in industries where the oil content would not interfere with its use.

Pine oil is a mixture of terpene alcohols, esters, ketones and other derivatives boiling mainly between 210° and 225°. The ordinary product has a gravity of about 0.940, although special products are put out of either higher or lower gravity. Its chief constituent is terpineol. About twenty different terpene derivatives in all have been isolated from it. It finds quite an extended use as a solvent, and also as a raw material for manufacturing or isolating various terpene products.

Tar, Tar Oils, Creosote Oils, Pitch, Light Oils, Wood Oils, Gas.—Whenever cellulose, lignocellulose or any variety of wood is distilled, we obtain gas, tar, and light oils. In the case of hard woods, the gas and tar are used entirely for fuel to aid in the distillation. Tar from hardwood has not so far been worked up into marketable products, with the exception of some of the light distillates of the tar known as wood oils, which have found a limited market in manufacturing shingle stains and similar products. When we distil a resinous wood, the decomposition products of the rosin are mixed with those of the wood. In this case the tar becomes naturally much more valuable. It finds a ready market as such, particularly in the rope-making industry, or it may be distilled and refined to produce tar oils, which find a limited market, particularly in the drug trade, creosote oils, which find a very fair market in special industries, and which should be largely used in preserving timbers, if the price of coal tar preservative continues to rise.

The light oils from resinous woods, which are between tar oil and turpentine in their character, find a very limited market.

The residue from distilling tar is pitch. You find this same residue in distilling rosin, and of course in distilling wood where the temperature inside the retort is properly controlled. Pitch is readily marketed both in this country and abroad.

These are the main primary products produced from wood utilization plants. It is obvious that no one plant can produce them all. If, for example, the rosin is extracted and sold as rosin, there will be no production of marketable tar and pitch.

Cattle Foods.—We have noticed that the cellulose of wood and possibly part of the lignin can be hydrolyzed rather easily to form glucose. There are of course a number of other sugars formed, the total from pine wood being about 23 per cent; from hardwood, possibly 26 per cent or more of the dry weight of the wood. In addition, there are other soluble carbohydrates and considerable quantities of unchanged cellulose and the lignin part of the molecule. A large part of the soluble carbohydrates are presumably thoroughly digestible, and as cattle are able to digest certain varieties of cellulose, it is possible that a certain percentage of the insoluble portion may be digestible. When this digested wood is mixed with cane syrup, peanut meal, rice meal, alfalfa, etc., it seems to make good cattle food and finds a market.

THE SECONDARY PRODUCTS.

Acetic Acid and Acetone.—Nearly all of the acetic acid and a very large part of the vinegar in this country is produced directly from acetate of lime by treatment usually with sulfuric acid and more rarely with hydrochloric acid. The acetate of lime is usually shipped from the point of manufacture to separate chemical plants for its further conversion. The manufacture of acetone in the same way is entirely dependent on the wood utilization industry. It is made exclusively by direct distillation of acetate of lime. This being the source of acetone, it follows that indirectly the manufacture of chloroform and iodoform are dependent on the same industry.

Camphor.—A number of processes lead from pinene, the chief constituent of turpentine, to camphor, and some of these at times have been placed on a commercial basis. When turpentine was fifty cents per gallon and camphor one dollar per pound, this was a profitable industry. When turpentine went to one dollar per gallon and camphor to fifty cents per pound, it was an unprofitable one. Today, so far as I know, camphor is not being made synthetically. Whenever there is a

rise in the price of camphor, or a decided improvement in the yields of camphor obtained, there is no reason why it should not again become an industry. On the other hand, if the use of camphor should decrease, due possibly to a more extended use of other materials in place of celluloid, it might never be a profitable industry again, even with low-priced turpentine and good yields.

Rosin Oils.—When rosin is heated in the neighborhood of 300°, or a little less, a steady and uniform decomposition occurs, giving water and light rosin spirits, and afterwards rosin oils. Some of these oils find extended use in the manufacture of axle grease and other lubricants, others in making printing ink. The pitch residue remaining in the still has already been mentioned. Rosin extracted from waste wood gives the same products, but unless the heavy oil mentioned above has been entirely removed from the rosin, the oils have rather a sharp odor, which must be removed before they can be used, for example, in printing inks.

A good many attempts have been made to devise a process by which resinous wood could be converted into paper pulp by the soda method, and the soda liquors which contain rosin distilled directly for the production of rosin oils. This can be done, and has been done in a small way, but the rosin oils obtained differ from the ordinary commercial product, being lighter in gravity and more mobile, and the process is not today a commercial success. In no case at present are rosin oils being manufactured in the primary wood utilization plants.

Wood Preservative and Paints, Disinfectants, Sheep Dip.—Tar is often a source of delight to the organic chemist, because it is so full of possibilities, but it is always a source of discouragement because of the difficulty of realizing those possibilities. Tar and its various distillates contain considerable amounts of cresols and their derivatives. It is fairly easy to obtain distillates which have good properties as wood preservatives, either for impregnation or, when mixed with pigments, for external application. It is also fairly easy to obtain distillates having about the consistency of linseed oil and which may be of value in certain external paints when substituted for the linseed oil in the paint. In either way, there is here a valuable source of wood-preserving material, and it has been utilized, although in a very small way, for a great many years, particularly in railway equipment. This same occurrence of cresol has led to a great variety of disinfectants for stables, for lavatories, for sheep dip, etc. Pyroligneous acid obtained from resinous wood is chiefly water, but it contains small amounts of acetic and formic acids, wood alcohol, acetone and cresol. This has led to its limited use as a preservative and also as a general disinfectant for stables, and for refuse generally. All of these no doubt have values, but up to the present there has been no uniformity in their manufacture or composition, and no particular volume in the amount of business. It is a promising field rather than a present industry.

Perfumes, Liniments.—Pine oil has been shown to contain terpineol, cineol, fenchyl alcohol, camphor, borneol, methyl chavicol, and a variety of other terpene derivatives. It contains nearly 50 per cent of terpineol, and as terpineol is used extensively in the perfume industry, pine oil has come to form one of the commercial sources of that product. Most of the constituents of pine oil also have mild antiseptic and local anæsthetic properties, and all products of the pine have always enjoyed a high reputation in cases of lung troubles. This has led to a large and increasing consumption of pine oil in the drug trade, and among the manufacturers of patent medicines.

Embalming Fluid and Specialties.—So long as products have not been thoroughly investigated they contain wonderful possibilities, and a great many plants on a basis of slight investigation have put out long lines of special products covering almost the whole range of human requirements, living and dead. These are so variable and there is such a lack of uniformity and precision in different cases that it seems useless to go into them in detail, particularly since we can hardly dignify it by the name of an industry as yet.

When turpentine or pine oil is distilled with steam, as is ordinarily the case in wood utilization plants, the condensed water holds a certain amount of terpene constituents in solution, and this condensed water has often been found of value as a mild antiseptic, and has been the basis also of the manufacture of embalming fluid.

THE VARIOUS PROCESSES.

Hardwood.—Originally wood was distilled in heaps covered with turf, a portion of the wood being burned to carbonize the rest. This was improved by substituting permanent kilns, usually of brick, for the turf. Where charcoal is the chief product required, these are still in extensive use. More than half the acetate of lime and wood alcohol are lost, however, if their recovery is attempted at all from kilns.

Three methods of distillation are at present used in this country, in addition to kilns: First, a vertical retort, the wood being placed in a basket, lowered into the retort and the charcoal removed in the same way after distillation. The retorts are quite small, and I have seen them only in New England. Second, the horizontal retort holding nearly a cord, and usually set in pairs. These are used largely in New York and Southern Pennsylvania. Third, the large, horizontal steel ovens approximately 60 feet long, where the wood is run in on cars and the charcoal is withdrawn soon after distillation is completed, and allowed to stand in coolers until it can be brought safely into the air. This type of plant is used largely in Michigan, and is the most efficient one now operating. The yields average about ten gallons wood alcohol, 200 pounds acetate of lime and 50 bushels charcoal per

cord of wood. Gas and tar are used as fuel for the retorts, there being very slight encouragement at present to utilize any of the tar or its distillates. Hardwood distillation has been repeatedly described in the literature, and further discussion here would not be profitable.

Paper Pulp.—So far as I know, only one plant is today manufacturing paper pulp on a commercial scale from what would be called wood waste. This plant started operation on planer shavings by the sulfate process. Some attempt has been made to recover turpentine and pine oil. A yield of forty or fifty per cent, computed on the dry wood, would be expected, and the paper made from the pulp so far has been chiefly a good grade of wrapping paper. A great many experiments are at present under way and a number of plants are projected, but today we must say that the industry has a future rather than a history.

Ethyl Alcohol.—In the two plants operating today the material is shortleaf or loblolly pine unselected waste from lumber mills. All the waste is ground and shredded, then treated in large rotating digesters with very dilute sulfuric acid at high pressure and high temperature for a short time. The digested mass is then extracted in diffusion batteries the extract purified and taken to the fermentation vats and the residue pressed to remove a part of the moisture and sent to the boilers. After the fermentation the liquors are distilled as usual to produce 95 per cent ethyl alcohol. The yield may be considered to be about twenty gallons per ton of material. This can, no doubt, be increased with improvements which would prevent decomposition of sugar during digestion and which will increase the percentage of fermentation in the presence of the large amounts of other extractive, unfermentable materials.

Destructive Distillation.—Of course hardwood distillation is destructive distillation. This present section refers to distillation of resinous woods. This has been conducted on the three chief varieties of resinous woods: Longleaf pine in the South, Norway pine in Michigan, Wisconsin and Minnesota, and Douglas fir on the Western coast. There are, and have been, a very large number of such plants operating with a great variety of retorts and kilns. By far the greater percentage have been unfortunate financially. A few have been operating continuously for years. The most important improvements in recent years have been in simplification of the process, reduction of labor costs and more accurate control of the temperature. Only rich resinous lightwood or stumps or sawmill slabs which are rich from having been chipped for turpentine, can be used profitably. Yields vary with the wood and with the plant. A fair estimate would be ten gallons turpentine, one to two gallons pine oil, one to two gallons very light oils containing most of the rosin spirits, fifty gallons tar, one hundred pounds pitch, forty bushels charcoal per cord. Of course these same products are often converted into other materials before they are marketed, but the figures given represent a fair estimate of what is obtained in a good plant. If the raw material is not too expensive, the plant well managed, the material properly prepared for the market, and the shipping facilities good, there is a margin of profit. The margin is not large enough, however, so that any of the above precautions can be neglected.

Steam Distillation.—When turpentine was seventy-five cents or more per gallon, the process of steam distillation alone was a real industry. To-day it is a part of history excepting in the case of two or three plants working on sawmill waste. In these cases where the sawmill waste costs nothing, the wood is chipped, extracted for a very short time with steam in retorts of which a great variety has been in use, and the extracted wood immediately conveyed to the power house. By a proper system of conveying and retorts, the cost of handling is very low. The cost of raw material may be considered as almost nothing, and the yield of a gallon or two of turpentine per cord and a little pine oil will show a profit on the investment.

Steam distillation plants for extracting lightwood in the same manner were quite common two or three years ago, but not one is now operating. It should be said in their favor that they were the first ones to produce good marketable turpentine extracted from wood, nearly approximating the gum turpentine, and they should further be credited in most cases with establishing their plants under the proper assumption that they were installing only a partial process which must be completed by the further extraction of rosin or other products before they could hope to be on a sound foundation. This, in a measure, is being realized in some of the solvent plants where turpentine and pine oil are recovered by regular steam distillation methods before the rosin is extracted. The same thing has been done in a small way with the paper pulp plants and the ethyl alcohol plants.

Bath Processes.—Two plants are now operating and have been for some years on what is called the bath process. In this system the wood is placed on cars and run into a retort and the retort is then flooded with a hot bath of high boiling material. This bath extracts the turpentine and pine oil and probably some of the rosin from the wood, and by driving steam through it the turpentine and pine oil are recovered, and the bath may be used over again. The bath may be made of rosin or of mixtures of rosin, pitch, tar, etc. After the wood has been extracted in this manner, such parts as are not needed for fuel are conveyed directly to destructive distillation ovens and distilled in the usual manner.

Solvent Processes.—Rosin is soluble in carbon bisulfide, carbon tetrachloride, alcohol, turpentine, gasoline, naphtha, etc. The chief solvent used in extracting so far has been mainly a grade of naphtha, the initial boiling point being not usually lower than 85°.

and all distilling below 120° or 140°. The wood, ordinarily lightwood or stumps, is chipped in an edging grinder, shredded, and placed in a retort. In some cases the turpentine and pine oil are then steamed off and the solvent added, while in other cases the solvent is added in the beginning. The former process requires more time, and as it leaves the wood moist, the succeeding extraction with solvent is supposed to be less efficient than in the latter case. On the other hand, if the solvent is added initially, the turpentine and pine oil become mixed with it, and a complete separation so that the turpentine contains none of the solvent is very difficult and in some cases commercially impossible. The solution containing rosin is concentrated, and finally the last of the oil is driven off with steam or superheated steam, leaving the rosin in good condition to market. Ordinary lightwood may be said to yield ten or twelve gallons of turpentine, two or three gallons pine oil, and four hundred to four hundred and fifty pounds of rosin per cord. Stumps will yield from six hundred to six hundred and fifty pounds of rosin, and proportionately larger amounts of turpentine and pine oil. Norway pine stumps usually yield about three hundred pounds of rosin.

There are at present at least eight plants in this country either operating or ready to operate by the solvent process, situated in Mississippi, Alabama, Florida, South Carolina and Michigan. The apparent difficulty is the loss of solvent amounting ordinarily to twenty or twenty-five gallons per cord extracted, and as the solvent used in most cases has increased very rapidly in price in the last two or three years, and is still increasing, this fixed cost becomes a very heavy charge on the plant.

Cattle Food.—This is allied to the ethyl alcohol production, but it stops with the hydrolysis of the cellulose. It has been in operation in England for two or three years, and a small plant has been operating in this country in Wisconsin for about a year. The hydrolyzing agent is sulfur dioxide and the conversion of material such as wood waste into food certainly looks promising.

THE PRESENT SITUATION AND TENDENCY.

In hardwood distillation the tendency is to the continued use of the large oven with cars like those used in Michigan. Improvements have been limited mainly to small ones giving slight increase in yield, and more attention has been devoted to simplifying processes of separating and purifying wood alcohol and acetate of lime. There is no rapid increase in this industry. The paper pulp production seems to be only in its infancy. There has been too much tendency to regard the manufacture of turpentine and rosin as the main operation of a plant with paper pulp as a by-product. This must be entirely reversed, and plants must be built where necessary particularly designed for the manufacture of paper pulp and the material must be selected for that purpose, and turpentine and rosin, where recovered, must be considered as by-products. The manufactures of ethyl alcohol and of cattle food must also be regarded as still in their early stages. The processes are similar in the first stage but of course are mutually exclusive. If the material is used for cattle food it cannot be fermented to produce alcohol, and vice versa.

In destructive distillation plants working on resinous woods, the tendency has all been in recent years to careful control of temperatures, simplification of process, and selection of wood. In this field more than in any other there is an opportunity for careful examination of the products and development of their use for special purposes. The only excuse for destructive distillation is the small cost of the plant and cheapness of operation. Aside from this it is much more rational to separate the oleoresins from the lignocellulose and treat each one in whatever way seems desirable. The number of destructive distillation plants does not seem to be increasing with any particular rapidity, but the ones that are firmly established seem to bring in fair returns from their operation.

Steam distillation alone as a method of treating wood is dead, excepting where the plant works on mill waste exclusively. If a mill is cutting longleaf pine, particularly timber that has been boxed, this forms a cheap and efficient installation and pays interest on the investment.

The bath process plants with succeeding destructive distillation of the wood have neither increased nor decreased in number recently.

Solvent process plants have increased very rapidly within the last year or two, but with lower prices of turpentine and rosin, and higher prices of solvent they are beginning to see difficulties ahead, and may find it necessary to change the character of solvent, or change the method of extraction.

Many schemes are floating in people's minds of combining various processes into one, for example, a combination of steam distillation solvent process and paper pulp, but these are still in the future. There is at present a very healthy interest in conservation in general, and in the utilization of wood waste in particular. It is a field that produces remarkable enthusiasm in the investigator, and if this interest and enthusiasm are controlled by a sane consideration of the difficulties in each particular case, a dispassionate review of former lack of success in similar or allied cases, and a willingness to learn from previous experience, there is no reason why the present tremendous waste in this field should not be converted into a large annual income.

Lime has dropped in price, "due to the concentration of the industry into larger units, with the consequent lowering of cost of manufacturing," according to the Geological Survey. The United States' output last year was 3,529,462 short tons—average price $3.06—against 3,302,015 tons, with an average price of $4.03 in 1911.

THE SCIENTIFIC ADVANCEMENT OF THE CANNING INDUSTRY.*

The preserving of foods has its basis in the work of Pasteur (1822-1895), but even 70 years before his researches we have, in 1795, a process invented by a Frenchman, Appert, for preserving foods in hermetically sealed receptacles, and this process was awarded a price of 16,000 francs by the French Government. This process consisted in placing the articles to be preserved in corked receptacles, and then subjecting these to the heat of boiling water for varying lengths of time dependent on the nature of the foods. Naturally this process of Appert was kept as secret as possible, but the information gradually leaked out, and in 1815 was brought from England to America. In 1819 an Englishman named Daggett had a canning factory in New York City for packing lobsters, salmon and oysters, and in 1825 fruits and vegetables were canned.

In these early days glass jars only were used, but their cost, breakage, etc., led to the use of tin cans, the first patent for which was secured in England in 1823, and in America in 1825. The cans were made in the canning factory, and their manufacture was slow but interesting. The greatest difficulty was experienced in making the tops and bottoms. A weight was pulled up to the ceiling and allowed to drop on a sheet of tin; a die was cast in the under side of the weight and the opposite die was cast in a piece of metal below. In order to guide the weight so that the dies would strike in the proper place, two upright grooved guides were made, similar to those of a pile driver. The body of the can was made on a cylindrical form the edges were butted together and soldered, and then the tops and bottoms soldered on.

Gradually, however, machinery was developed for can-making, and today the process of production of finished cans from sheet tin plate is automatic and continuous, and the industry is entirely separate from that of canning, although many canning companies work their own can-making plants.

In the original Appert process only boiling water was used for sterilization of the foods. This was found insufficient for many products, so, later on, salt was added to the water to raise the boiling point, and this was afterwards supplemented by the addition of calcium chloride, so that temperatures, up to 240° F. could be produced. In 1874, a Baltimore man invented a closed retort for cooking with superheated steam. This led to our modern retorts or autoclaves, which produce various temperatures from 212° F. up, depending on the steam pressure used.

Although the industry dates back to 1795, it was conducted for a long time entirely without any knowledge of the real scientific principles underlying the methods in use, and it is interesting to look at some of the early theories advanced. The first theory was that of the early exclusion of air. This was recognized by Appert, who stated that it was the external air which caused spoilage and not the air in the jar. Guy-Lussac, who was instructed by the French Government to investigate Appert's process, reported that spoilage of food was caused by a series of oxidation changes, and by drawing out the air and preventing its getting in again these oxidations were prevented. This theory that the air must be excluded was followed up to recent times, in evidence of which we see, only a few years ago, that cans were sealed, heated, vented to allow the air to escape, resealed and then cooked. Sometimes a second heating and venting was given before cooking.

The next theory was the vacuum theory, closely related to the first theory; that is, it was believed to be only necessary to get rid of the air by vacuumizing and mechanical methods were developed to produce a vacuum. Many losses were experienced by those who blindly accepted this theory, for the vacuum has no real value in preserving foods, except in special instances such as salt meats, peanut butter, jams, etc.

Pasteur was the first to associate spoilage with organism. Russell, of Wisconsin, was one of the first to apply the theories and methods of Pasteur to the solution of spoilage problems encountered in canning, and in 1895 he showed that spoilage in canned peas was due to the presence of bacteria which had survived an insufficient sterilization. Prescott and Underwood, of Boston, made studies of sour corn, and first explained to the Packers' Association Convention at Buffalo, in 1898, some of the causes for spoilage in canned foods, and they showed slides of bacteria they had isolated from sour corn.

Among the important early investigations on canned foods was the work of the Canadian Government in 1897 on the spoilage of canned lobster. The packers were troubled by so-called "black lobster," and the investigation showed it to be due to bacteria.

With the introduction of science into the industry the first step was to put the processing or sterilization on a sound basis. This entailed a careful study of the organisms found on fruits and vegetables and in the air. By the introduction of these organisms into good cans the changes produced were noted. The temperatures necessary to kill these organisms were studied. The time necessary for heat to penetrate to the center of cans of food of different consistency was found out. By adding to this time of penetration the time necessary to kill the bacteria the basis of a process was established.

One of the instruments, used very largely nowadays for determining the necessary time for heat penetration, consists of a can, procurable in any desired size, fitted with a gasket which is easily screwed to the can by means of the wrench. A self-registering thermometer is attached so that the bulb is in the exact center of the can, for this is the point to which the

* From the Journal of the Society of Chemical Industry.

heat must penetrate to ensure complete sterilization. The mercury in the thermometer is shaken down, the can filled, sealed, and put through the process with the other cans. It is afterwards opened, and the maximum temperature reached is read on the thermometer. Another form of instrument is a can fitted with a thermo-couple. Wires lead to a recording instrument outside the can, and the progress of the temperature is recorded on a chart. By experimenting with these cans, valuable data may be obtained for different temperatures, times, etc. The processes which were successfully used years ago are now unsafe, because as time goes on larger numbers and more resistant kinds of organisms have to be dealt with.

During this study of micro-organisms it was discovered that weather conditions affected the bacteria on the crops, that uncleanliness and delay in handling raw materials meant the multiplication or the introduction of undesirable organisms which were very hard to kill. Hence processes are varied slightly with weather conditions, and every packer guards against bacterial multiplication by the rapid and careful handling of all his products, otherwise excessive temperatures would be required, and of course the longer and more intense the heat, the less presentable is the finished product.

By this careful study of organisms and the changes brought about by these organisms in different classes of canned foods, two distinct divisions have been made in sterilizing. It was found that the spores of spore-bearing organisms are very difficult to kill; in boiling water they could survive for hours, but that 10 to 15 minutes at 240° F. usually killed them; it was also found that these spores would not develop in media having an acidity above 0.3 per cent. On the other hand, yeasts, molds, and some non-spore bacteria were able to grow in a moderately acid medium, but were easily killed in boiling water. Hence, when any foods of high acidity, such as fruits (and tomatoes), are canned, it is usually in boiling water for varying lengths of time, while the non-acid products (vegetables) receive temperatures above 212° F. in order to kill the spores. This then is the line of division between the use of the open bath (or boiling water and the retort or temperatures above that of boiling water).

When the packer became aware of the many possibilities of loss, he introduced a system of testing his products now known as the incubation test. A room is maintained at a constant temperature of 98° F., and from each cook a few cans are taken, carefully marked and placed in this room for about five days, when any unskilled organism will have had time to develop. The cans are then examined physically and microscopically, and if anything abnormal is found, the corresponding batch, which will still be in good condition, is located in the warehouse and the goods are discarded or retreated, depending on their condition and the cause of trouble. Thus the packer is able to put his products on the market with a reasonable assurance that they will keep, but of course occasional cans may later develop a leak and the contents be spoilt. It is essential in this work to have the room maintained at 98° F., because most organisms with which we are concerned develop best at this temperature, while some develop slowly at temperatures above or below this.

By testing the finished products in this way, many irregularities have been noticed, and arriving at the cause of all cases of spoilage has led to many improvements in methods of sterilizing. Thus, it was sometimes found that the cans had been put in and never cooked, or else the time had been forgotten and the cook cut short. To overcome this, different forms of clocks which show the time, etc., on each cook are now used. Some of these are automatic, and shut off the steam at the proper time. In other cases where only part of a batch was spoiled, it was found that uneven temperature conditions existed, and hence the introduction of modern steam regulating and circulating devices.

One of the early difficulties encountered by the bacteriologist was the differentiation between a leak and a swell. To the layman this might seem simple, and of course in the case of a visible leak it is easy, but most of the leaks are so minute, and being on the seam or in the solder, they cannot be found. Organisms have entered these small holes, and the cans swell. The hole becomes cemented up with the contents of the can, and the foods or gases do not leak out. Sometimes a small hole will leak from the outside in, but not from the inside out, sometimes these holes are closed more firmly by the strain on the can. It became necessary then to make a bacteriological study to distinguish the cans spoiled by a leak and those spoiled by under-treatment, and we now have a very reliable distinction which was arrived at by a careful study of cans known to be under-treated, and those known to be leaking. I explained that in non-acid products it is necessary to not only kill the bacteria, but also the spores, which require a great heat in most cases. If therefore in a swelled can of food of low acidity we find only living spores or spore-bearing organisms, it is safe to say that the can has not been sufficiently sterilized; on the other hand, if we find lactic acid bacteria present we know that the can leaks. This conclusion is very sound; the lactic acid bacteria are very prevalent in the air, they are very minute and can pass through a very small hole, and they are the first organisms to seize on any matter containing sugar; hence if any air is drawn into the can through a small leak these lactic acid organisms will be present. There may be others too, but the presence of living lactic acid bacteria is proof of a leaky can.

In the case of the acid products, the differentiation is not so easy, and requires considerable experience and judgment. As I said, the spores do not develop in this class of foods, only the yeasts, moulds, and some

non-sporing bacteria, and in an under-treated can we find some one of these present in pure culture, while in a leaky can there are several varieties of each or all.

These conclusions are drawn of course only when the cans have been subjected to a fair degree of heat, which is ascertained by a physical examination of the contents and the can. For instance, in tomatoes, when a fair amount of heat has been applied, the gelatinous envelope surrounding the seeds will be removed; in the case of fruits, the color, softness, etc., is an indication of the degree of cooking. In the case of foods given a heavy treatment, as is necessary for vegetables, the inside of the can will have a bluish cast and galvanized appearance.

Besides the bacterial examination of swelled cans, it is customary to empty the can, clean in hot lye, reseal, and subject it to a pressure test under hot water. Very frequently minute holes are found in this way, but the method is not so reliable as the bacterial examination, for some leaks become cemented so firmly that they can withstand high pressure.

An examination of the gases present also aids in this work. In all cans there is a certain amount of head space, and the gas in this head space would be expected to consist of the constituents of the air, plus any other gases formed in the sterilizing, but it has lately been shown that changes take place whereby practically all the oxygen in cans or fruit disappears, and only nitrogen, hydrogen and carbon dioxide remain. This disappearance of oxygen is accounted for by the formation of oxides with the tin and iron; by the oxidation of iron and tin compounds; or by combination with hydrogen which is formed by the action of the acid on the tin plate. The hydrogen does not appear in this head space until all the oxygen is consumed. In the case of vegetables we may have sulphuretted hydrogen and phosphoretted hydrogen formed by the breaking up of the protein matter under the high heat, along with nitrogen and possibly some carbon dioxide and oxygen.

Now let us look at spoiled cans. In the case of a leak a large proportion of free oxygen would be found; in the case of a swell in fruits we would find the regular gases of alcoholic fermentation (carbon dioxide and hydrogen); in the case of swells in vegetables due to under-treatment we find large amounts of foul gases such as sulphuretted hydrogen, phosphoretted hydrogen, etc.

You can see therefore that the examination of the gases in conjunction with the bacteriological examination is a valuable aid in determining the cause of spoilage.

An instrument for drawing off the gases from a swelled can consists of a hollow needle for puncturing the can. A rubber stopper makes a tight joint to prevent gases escaping at the hole. A screw presses the plate up and forces the needle through the can, the gas being led off through the needle to a collecting apparatus. A later type of instrument has an auxiliary tube to force water into the can, and thus drive all the gases out for quantitative work.

In the canning industry we use certain terms in describing spoiled cans, namely leaks, hard swells, flat sours, and springers. A leak is one where the food is spoiled by the entrance of organisms through a small hole. Sometimes these holes are visible, especially if due to the faulty capping of the can, but more often the leak is invisible. By a hard swell is meant a can which is swelled out perfectly tight by the gases envolved in the spoilage, and no amount of pressure will force the can back to normal size and shape. This class represents an advanced stage of spoilage, and when the pressure generated inside becomes sufficient the can bursts at the weakest part, usually on the seam. A hard swell in vegetables is usually foul smelling, due to the malodorous gases formed in the breaking down of the vegetable matter by the spore-bearing organisms: a hard swell in fruits does not give foul gases, but only the ordinary gases of alcoholic fermentation. Generally speaking, hard swells are the direct result of under-treatment.

By flat sours are meant cans which, to outward appearances, are perfectly normal, but when opened contain foods which are very sour or bitter. This occurs in corn, peas, beans, pumpkins, tomatoes, etc. They may have gone sour previous to being packed, but this condition is rare. The principal cause is under treatment; the bacteria bringing about this result are spore bearing; they generate practically no gas; are anaerobic, and hence live on the carbohydrates, producing lactic acid. They are rather slow to develop, and therefore spoilage may not show for months, but if the incubator test is used, the spoilage will develop in about 10 days at 98° F. From the fact that the cans are outwardly of good appearance, this class of spoilage presents great difficulties to the packer.

When parts of a pack get into this condition, it is a matter of careful and painstaking work to separate the good from the bad, and even when all care is exercised, the methods used are not entirely satisfactory. One method is to put the cans into boiling water, bottoms up. The expansion of the contents causes the ends to snap out, and of course the sour cans snap out first. By frequent cutting of the cans during the heating, a time is arrived at between the snapping out of the sour cans and of the good ones. Another method is to heat the cans until they all snap out, then cool them, and separate the good cans which snap back first. The success of either method depends largely on the operator, and is only approximately correct, because other factors, such as variations in filling, exhausting, etc., of the cans affect the separation.

Springers are those cans where the vacuum is broken, the ends have sprung out, but may easily be

pushed back again. This condition sometimes exists in vegetables, but in this class of foods a springer will likely develop into a hard swell. The most frequent trouble with springers is in fruits and tomatoes, so the term applies particularly to these. There are two subdivisions in springers; those in which are living organisms and those in which no living organisms are found. If living organisms are found, tne trouble may be due to a leak or under treatment, and if the latter, a hard swell would probably develop later on. Some springers, however, have no living organisms. The action of the acids on the tin plate envolves hydrogen and if there is very little space in the can, the gas when expanded by heat causes the ends to flip out, hence cans should not be filled too full; sufficient head space must be left for the expansion of the gases present. Another cause may be insufficient exhaust, i. e., the heating of the foods before of after they are in the can and previous to capping. This is done to expand the contents and drive out the excess air. The cans are then sealed at once, heated, and after cooling there is a contraction, and the ends of the can are drawn back into place. If the exhaust is insufficient, the end will not draw back properly. Another cause of springers is when fruit seeds or stones are present, and their seed life has not been killed, a development of the embryo will have taken place, with production of carbon dioxide in sufficient amount to cause the ends to flip out.

Discolorization in canned foods.—Much trouble is encountered due to loss of color or development of undesirable colors in fruits and vegetables, and many of these troubles have been accounted for. The color of such fruits as strawberries, raspberries, and cherries is very delicate and easily destroyed. It was found that some of this was due to the action of the acid on the tin plate, iron compounds, which darkens the fruits, being formed. In other cases the fruits lose their color altogether, and as far as I know, there is no explanation of this, except that the chemical compound constituting the color is destroyed by the heat. Light colored fruits, such as peaches, pears and apples, sometimes turn pinkish or brownish. As this may develop in enamel cans, plain cans, or glass jars, the cause must be chemical; the brown color is due to caramelization of the sugar by overcooking, but what the pink color is due to is unknown; it is probably an early stage of this caramelization.

Another frequent cause of trouble in white fruits is the presence of black spots. In preparing fruits it is necessary to immerse them immediately in water or dilute salt solutions to prevent them from turning dark by exposure to the air. Sometimes a very dilute sulphite solution is used to retain the color, this afterwards being washed off. However, sometimes a little sulphite remains on the fruit; then if there should be any appreciable amount of iron in solution, either from the tin plate, the knives used in peeling, or from the water, black iron sulphide is formed under the effect of heat, and hence the black specks.

In the case of vegetables the greatest difficulty is experienced with dark corn, and there are several reasons for this. This article is subjected to very high temperatures as much as 250° F. for 60 minutes. If the corn is not cooled rapidly there will be a marked discolorization due to caramelization of the sugar. The most frequent trouble, however, is from black iron sulphide formed by the combination of iron and sulphur. Discolorization of this kind is most frequent on the cap end or along the seams; the iron is usually derived from the tin plate by the action of the acids liberated from the flux by heat. The iron might also originally be present in the flux, or in the water. The sulphur is present as sulphuretted hydrogen, formed by the breaking up of proteid substances.

In the green vegetables such as peas, beans, etc., we have loss of color due to the destruction of chlorophyll by the heat. To overcome this, the French usually treat the peas with copper sulphate, but this method is not used extensively in Canada or the United States. Other methods have been proposed for preserving the color, and these aim to fix the chlorophyll as an insoluble compound on the vegetables. Such methods employ solutions of salts of calcium, barium, or strontium, but their value has not yet been proven.

The question of how to retain the natural color of fruits and vegetables presents a good field for research, especially in the case of vegetables.

Canning of peas.—Last year's pack of peas ranked third in importance in the United States; the quantity packed amounted to a little over 7 million cases or 168 million cans (the largest pack was tomatoes, 14 million cases; then corn, 13 million cases). Modern harvesting is done entirely by machinery, the vines being cut about the same way as hay. Special machines called viners, handle the cut vines, removing the peas from the pods by heaters. The peas fall through perforations in a cylinder, large enough to allow the peas to pass through, but which retain the vines, pods etc. Sometimes these viners are placed in the fields, but more often the farmer hauls the vines to the viners at the factory. The peas from the viners are next washed in cold water, in a revolving squirrel cage, to remove all the dirt and some of the mucous substance which adheres to the peas. The next step is the grading, which is also done in an inclined, revolving squirrel cage. These cages are perforated in sections, with different sized holes, the first 9/32 in. diameter, through which pass the "petit pois"; the second size 10/32 in., giving the extra sifted peas; the third size, 11/32 in., the No. 3 or sifted peas; the fourth size, 12/32 in., the early June peas; those that pass out at the end are marrowfats or standards. Some packers, however, only produce three grades, and arrange the sections of the grader accordingly. There

is also a method of grading peas for quality according to their density by using different strengths of salt solutions. The first grade floats in a solution of sp. gr. 1.040, the second grade sinks in this solution, but floats in a solution of sp. gr. 1.070, while the third grade sinks in the latter. This grading for quality coincides very well with the grading for size After the peas are sorted or graded, they pass over a wide belt, on each side of which are seated women, who pick out the foreign material and the broken and defective peas. The next operation is the blanching, the object of which is to remove the mucous substance from the peas, and to drive water into the peas so that they will be soft and tender. This is done in boiling water for from 1 to 12 minutes, depending on the peas. It is one of the most important steps in the handling of peas, and requires experience and good judgment. The machines for blanching are of the squirrel cage type revolving in water, and the speed can be varied to deliver the peas at the outlet in the proper time required. The water flows in the opposite direction to the motion of the peas, so that as the peas come out they receive clean water. The peas after blanching are washed with cold water, and then go to the filling machines, where they are automatically filled into the cans, the brine of salt and sugar being added at the same time. The cans are then capped by machinery, heated in retorts at 230° to 240° F. and 25 to 40 minutes, depending on the quality of the peas, then the cans are cooled and stored away. Delay may mean production of sour peas, or multiplication of bacteria, which would not be killed in the process, and would produce swells.

A most desirable quality in canned peas is to have them open up with a clear liquor. Very frequently the liquor is milky or cloudy.

Examination of this cloudy liquor shows it to have a high content of starchy material; that is, the starch has passed from the peas to the brine. This may come about by over-cooking, which would break the peas; by not properly cooking the peas after heating, which would allow a slow cook to go on; by improper grading, when the smaller peas would be overcooked; by mashing at the filling machines, or overfilling the cans, when the expansion would mash the peas. If the peas are not properly blanched to remove the mucilaginous matter, this will cloud the liquor. If there has been any heating (sweating) of the peas previous to canning, the liquor may be cloudy, because of the slime produced by the bacteria, and this slime is very difficult to remove by washing or blanching. A most frequent cause is the canning of over-mature peas, when the starch content is higher than in young peas. All these points, however, are dependent more or less on the skill and care of the processor.

Even with careful watching of all these points we may have cloudy liquor, but the causes are more of a chemical nature. For instance, if the water that is used is very hard, the lime and magnesia combine with the albumins, forming insoluble albuminates, which give the peas a thin hard shell which will not expand in the heating, but cracks and allows the starch to pass through into the liquor; the water itself might also become cloudy due to precipitation of the temporary hardness. It becomes necessary therefore to have a good supply of soft water, and in many places the water is purified to overcome these possibilities.

Some seasons, and in some districts, the peas are high in starch, and it is almost impossible to obtain clear liquor. A means for converting the starch into a soluble compound by means of an alkali such as sodium carbonate suggests itself. There is also the question of the solubility of protein matter in water, salt, and sugar solutions, the protein of the pea is more soluble in salt solution than in water. Experiments in Germany indicate that the use of excess of nitrates as fertilizers produces peas which tend to give cloudy liquor.

Tin Plate.—The canning industry calls for the use of large quantities of tin plate for can making. This plate must be of good quality, free from pin holes. The estimation of tin in tin plates presented many difficulties, but we now have reliable methods. A neat method for the detection of pin holes and imperfections in plate consists in coating the plate with a solution of gelatin, potassium, ferricyanide, and sulphuric acid. At the end of thirty minutes the pin holes or scratches are located by the blue spots due to the interaction of the iron and potassium ferricyanide.

Some food laws not only specify the amount of tin on the plate per base box, but also limit the amount of tin which should be present in the foods. This, of course, entails frequent examinations for tin, which in the presence of so much organic matter is very difficult. This question of solution of tin by the contents of the can is very important. Many people believe that old canned foods are undesirable because they contain too much tin; but recent investigations show that such a procedure is unnecessary and of no value; if the contents remain in an opened can, very large amounts of tin go into solution, and for this reason cans should be emptied immediately after opening. The cause of this excessive solution of tin is the oxygen of the air. As already shown, in sealed cans the oxygen disappears in a short while, and along with this disappearance of oxygen the solution of tin practically stops. The maximum amount of tin goes into solution in about three months, and after that there is very little change. The U. S. Department of Agriculture is investigating in California the question of effect of age on canned foods, and their results show that canned foods which have been packed for some time are actually better than those only packed a short while, and therefore the dating of canned foods would not be of any great benefit.

Solder.—The solder must be clean and free from dross, for the presence of the latter means pin hole

leaks. It must also be free from excessive arsenic and antimony, which would affect the flow, and if introduced into the food would be harmful. At present there are two principal grades of solder used: 40 parts tin, 60 parts lead; and 45 parts tin, 55 parts lead. Until recently solder was supplied in form of wire or cable, which was fed to the irons automatically. In the recently introduced solder-hemmed caps, the solder is in the form of a ribbon on the edge of the caps. This presents a great saving in solder and labor.

Flux.—The requirements of a flux are that it must be free from iron, and it must not be acid; also sal-ammoniac in any quantity is not desirable. At present a neutral zinc chloride solution free from iron is found best; resin, dextrin, oils, and other organic substances are also used, but they are not very good as they gum up the cans.

Water.—A very important item in the canning factor is the water. Nearly all the factories are in small towns or villages where the only supply is from wells. The water should be free from pathogenic organisms, because although any pathogenic organisms are killed in the sterilization, still some non-pathogenic organisms which would be hard to kill might be introduced. The water should be free from iron; aeration of the water, with filtering or settling, is usually sufficient to eliminate it. Water high in lime and magnesia forms insoluble compounds with albumins, thus tending to harden vegetables, and where these waters are encountered a purifying system should be installed.

As regards the question of scale in the boilers, latest figures show that a one-sixteenth scale increases the coal consumption by 12 per cent; so in the case of excessive scale-forming waters, boiler compounds are used. However, as so much live steam is used, coming in direct contact with the food, most boiler compounds are objectionable, and hence purification outside the boiler is resorted to.

Salt.—Large quantities of salt are used for brines in vegetables, etc., and this salt must also be free from iron and much calcium and magnesium salts. Magnesia may also cause undesirable bitterness of the brine.

Paste.—In the past, considerable trouble has been encountered with rusty cans, due to the paste used in attaching the labels. There are now good pastes which do not rust the cans nor soil the labels.

Sugars.—Only pure granulated sugar is used in canning, and fortunately this is always offered in high grade. For syrups I do not think there is any appreciable difference between cane and beet sugar. If beet sugar is properly refined (freed from raffinose) there is no chemical difference between it and cane sugar. The only difference is in the grain and color, but these are hardly sufficient to cause any trouble. Beet sugar usually forms more foam than cane, but this, I think, is due to the fineness of the grain rather than to anything else.

Miscellaneous.—There are numerous miscellaneous products used such as coal, vinegar, spices, disinfectants, washing powders, etc., all of which are tested in the laboratory.

Gauges and thermometers must be regularly tested. The steam gauges must be correct to avoid explosions, and the thermometers must be correct to avoid losses in cooking.

Sewage disposal.—In the past every effort has been made to eliminate any nuisance from this source, the solid particles being removed by screening, and returned to the land for their fertilizing value, the screened effluent consists of the washings from fruits and vegetables, and contains large amounts of nitrogenous matter; in dry seasons there may possibly be some putrefaction which is not harmful to health but may produce objectionable odors. Now that the Provincial Board of Health regulations prohibit all sewage or factory effluents from being poured into streams without purification, it will be necessary as time goes on and occasion demands it to put in purification systems, possibly on the lines of the septic tank and filter beds.

Utilization of waste products is not overlooked in the canning industry. The small fruits, trimmings, etc., are sometimes extracted for their juice for fountain syrups.

The apple wastes such as peelings and cores are either dried and sold for wine and vinegar purposes, or else the juice is pressed out and sold as cider, or made into cider vinegar. Unfortunately the demand for cider vinegar in Canada is not sufficient to allow of the profitable treatment of apple waste for this purpose. However, it is very profitably turned into apple jelly to be used as the base for compound jams. When these wastes are properly handled, no objection whatever can be taken to their use.

In pea canning large quantities of pea vines are left over, which make very good ensilage. Some factories have their own silos, and sell the ensilage in the winter, while others allow the farmers to take the vines away free of charge; in other places it is necessary to pay to have them carted away.

In corn canning there are large quantities of corn silk, a small part of which is used to make extract of corn silk for medicinal purposes. The use is limited, however, but we hope some day to find a large and profitable outlet for corn silk. The corn stalks, corn cobs, and husks, make good ensilage. The question of production of alcohol has been investigated but it was found that the recovery of alcohol would hardly pay for the cost of installing a plant.

Large quantities of seeds from tomatoes and pumpkins, as well as the stones, etc., from cherries, plums, and peaches, are now being utilized for their oil.

Many companies now have experimental farms, including several in Canada carried on by the Dominion Canners, the largest of which, situated near Brant-

ford, is about 1,000 acres, and is devoted entirely to seed production.

In the modern factory equipments the effect of the laboratory can be seen. The old retorts are being supplemented by ones in which the cans are agitated, thus shaking the contents and lessening the time of penetration of the heat, cutting down the time of sterilization, and giving improved flavor and appearance.

No doubt the future will see the more general adoption of the intermittent system of sterilization, that is, instead of sterilizing in one operation at a high heat to kill the spores, the sterilization will be accomplished in two operations at lower temperatures; the first will kill all organisms except the spores, then in two or three days these spores will have developed, and a second heating will kill these developed organisms. This of course entails handling the product twice, and hence would be costly, but no doubt can be worked on a small scale, and the increased quality and appearance of the goods will bring a higher price.

In place of the old iron pipes and iron parts on cookers, filling machines, etc., there are now copper, brass, enamel, or silver. In place of the old wooden floors is concrete, and in place of the old wooden top tables, enamel or even glass tops; in fact, everything is arranged so that a hose can be turned on and the factory washed out very rapidly.

In Germany the canners subscribe to a large laboratory and experimental factory; in the United States there are many private laboratories, and now a laboratory under the Canners' Association is to be started. In Canada, the Dominion Canners are the largest corporation, and they have their own laboratory and experimental departments.

The canning industry makes it a practice to investigate all the reports as to alleged ptomaine poisoning due to canned foods, and in practically every case gets a denial of the charge. A ptomaine is described by Vaughan and Novy as "an organic chemical compound, basic in character, and formed by the action of bacteria on nitrogenous matter," or, in other words, it is a putrefactive alkaloid, a product of decomposition. There are many known ptomaines, but very few of them are really poisonous. The poisonous ptomaines may be formed by pathogenic organisms, but a few yeasts and moulds, and a few anærobic spore-bearing organisms, all putrefactive in their action. There must be putrefaction to get poisonous ptomaines, and no packer would think of packing putrefactive products, so the only possibility arises where a can has leaked or swelled. Of the hundreds of reported cases of poisoning from canned foods, I only know of one where the charge was proved, and that was from a can of salmon that had a pinhole leak, and the consumer should not have eaten the contents, which were abnormal. Physicians and others should be very careful before diagnosing a sickness as due to ptomaine poisoning caused by eating canned foods; an injury is being done to a large industry, and the public is needlessly scared.

Canned foods are generally regarded as non-perishable products, and are consequently put into a shed or damp cellar which is not fit for anything else. The result is that the labels are discolored, the cans rust, and pinhole leaks result. Although freezing does not materially alter the flavor of canned foods, it is not advisable to allow them to be frozen, for when they thaw out the cans sweat and rust very easily. All canned foods should be stored in a dry place, of even temperature, with good air circulation around and underneath the pile.

WOOD ALCOHOL IN GERMANY.

There are no statistics available which would indicate the exact production of wood alcohol or its by-products in Germany, but a reliable estimate made several years ago places the annual output of wood alcohol in Austria-Hungary and Germany on the basis of 100° purity at about 6,500,000 kilos (14,330,000 pounds). Separate figures for each of the above-mentioned countries were not obtainable.

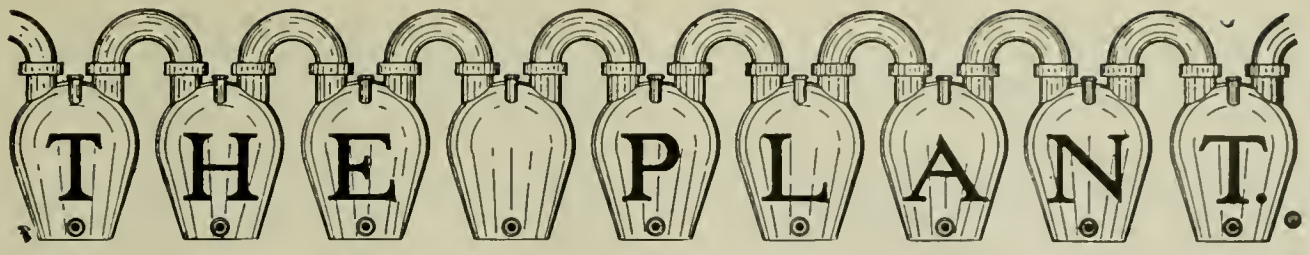
In 1912 Germany imported 9,398 metric tons (metric ton = 2,204.6 pounds) of crude wood alcohol, having a total value of $1,453,942, against 8,759 tons, worth $1,355,170 in 1911. Of these imports the United States supplied 4,319 tons in 1911 and 3,739 tons in 1912. Germany also purchased last year 912 tons of crude acetone from Austria-Hungary, the value of which was $184,450, the corresponding figures for 1911 being 767 tons and $155,175.

THE EXPORT TRADE—PRICES.

Exports from Germany of crude wood alcohol and acetone aggregated 263 tons, value $47,600, in 1912, in contrast to 766 tons, worth $139,940, in 1911; and the Empire also shipped to other countries 4,602 tons of refined wood alcohol, acetone, and formaldehyde, value $941,052, in 1912, as compared with 3,954 tons, value $802,060, in 1911. German statistics do not classify refined wood alcohol, acetone, or formaldehyde separately, but it is estimated that of the exports of these products in 1912, 41 per cent was refined wood alcohol, 22 per cent acetone, and 37 per cent formaldehyde.

The price of refined wood alcohol f. o. b. Berlin in usual wholesale quantities for August, 1913, was 166.50 marks per 100 kilos (18 cents per pound). Crude wood alcohol was quoted at 65 marks per 100 kilos (7 per cent pound). Of refined acetone the prices f. o. b. Berlin ranged from 145 to 160 marks per 100 kilos (from 15.6 to 17.3 cents per pound) according to quality.

A large ice-making and refrigeration plant is to be built at the outer harbor of Los Angeles, Cal., to supply ice for harbor purposes, icing ships, etc., and to furnish cold storage facilities at the harbor.



A STUDY OF THE OXIDATION OF COAL AND OF THE PROCESS OF COMBUSTION.*

By HORACE C. PORTER.†

It is well known from the work of several investigators in European laboratories‡ and from earlier work at the Bureau of Mines that all coals unite with oxygen more or less at ordinary temperatures. The action is at ordinary temperatures largely a simple addition, very little gaseous products of combustion being produced. There is, however, a development of heat by the simple addition of oxygen, and this heat development is the primary cause of spontaneous combustion.

As the temperature rises, the oxidation reactions increase rapidly in rate, and the simple addition reaction becomes complicated with the development of water and oxides of carbon as products of the oxidation and with the production of water and of methane and other gases by destructive distillation.

Under whatever conditions coal burns, as for example on the fuel bed of a boiler furnace or in suspension, as dust in the air of a mine, the earlier stages of oxidation proceeding at the lower temperatures have important bearing on the ease of ignition of the fuel and the degree of inflammability of its dust. In order to throw more light on the nature of the combustion reactions at successive stages and to determine how the various kinds of coal differ in their rates of reaction with oxygen, a laboratory study has been made of the oxidation of coal, at temperatures ranging from 80° to 300° C.

A series of experiments has been run with samples of different coals placed in atmospheres of pure oxygen at a pressure reduced so as to equal the average partial pressure of the oxygen in air. The rate of absorption of oxygen by the coal was determined by admitting pure oxygen at such a rate as to maintain constant pressure in the apparatus. Large differences in rate were found between different kinds of coal, and the comparative oxidation rates thus found conform in general to the known comparative degrees of inflammability of these coals.

At temperatures above 200° C. the production of CO_2 and other gases causes a considerable error in an experimental method which does not remove these gases as they are formed. A rapid-stream method was therefore devised in which weighed samples of dry coal were heated at definite tempratures in a rapid stream of dry air for one hour, the change in weight of coal being accurately determined as well as the amounts of H_2O, CO_2 and CO produced. From these data the total oxygen used and the oxygen fixed were calculated.

It was shown that the oxidation of coal consists in the earlier stages of the formation of an unknown complex of the coal substance with oxygen, and the more or less gradual dissociation of this complex as the temperature rises into water, CO_2 and CO. Below 200° water is the chief product of this dissociation, the proportion of CO_2 in the products increasing as the temperature rises. Carbon monoxide is a primary product of the oxidation of coal at temperatures between 100° and 300° C. and possibly also outside of this range. Triangular diagrams representing the relationship of the three products H_2O, CO_2 and CO at different temperatures show interesting tendencies, e. g., toward constancy in ratio between CO_2 and CO within a certain temperature range.

The production of water by oxidation of coal at 100° C. or lower is of interest in connection with the devising of methods for accurate moisture determination in coal. The direct production of CO at moderate temperatures is of interest in connection with mining operations and the storage of coal.

*Address delivered at the annual meeting of the American Chemical Society, Rochester, N. Y. Sept. 9-12. Published by permission of the Director of the Bureau of Mines.

†Chemist, Bureau of Mines.

‡Boudouard, Fayol, Richters, Anderson and others.

An attempt is being made by the Development Commissioners of England, through the University of Leeds, to revive the flax-growing industry in Yorkshire. Through the efforts of Prof. Priestly, of the botany department of the university, about 120 acres of land near Selby were sown this year. The university has also arranged to rent an abandoned mill at Selby for three years, to be fitted up for preparing the flax for market. This central retting depot was procured to insure the farmers that their efforts would be devoted only to growing flax. At one time the district raised great quantities of flax, and as late as 1896 (according to the press) 1,000 acres were grown in that region. The industry passed out here with the development of cotton, and flax spinning has disappeared from Leeds, where it stood first for a long time.

THE DISTRIBUTION OF HEAT IN THE OPERATION OF STEAM BOILERS.*

By PERRY BARKER.†

In the process of combustion of coal in boiler furnaces a comparatively large percentage of the heat in the fuel is not usefully employed for the generation of steam. The extent of the losses which ultimately affect the boiler efficiency is governed by (a) the design and physical condition of the plant, (b) the personal element in the operation of the boilers and furnaces, (c) the character and adaptability of the fuel for the plant in question, and (d) the rate of steam generation or capacity at which the boiler is operated. The efficiency with which fuel is burned is controlled by these factors, and excessive losses may be due to one or a combination of the contributing causes.

In accordance with the recent recommendations of the Power Tests Committee of the American Society of Mechanical Engineers, a balance accounting for the distribution of heat in a pound of dry coal fired consists of the following items:

I. Heat absorbed by the boiler.

II. Loss due to evaporating and superheating moisture in coal.

III. Loss due to evaporating and superheating moisture formed by the combustion of hydrogen and distillation of oxygen-hydrogen compounds in the coal.

IV. Loss due to heat carried away by dry flue gases leaving the boiler.

V. Loss due to heat escaping through the formation of carbon monoxide (CO).

VI. Loss due to combustible removed from ash pits and from grates during cleaning.

VII. Loss due to superheating moisture in the air used for combustion.

VIII. Loss due to unconsumed hydrogen and hydro-carbons, to radiation and unaccounted for.

Of the items enumerated above, IV, V and VI generally constitute about 75 per cent of the total heat which is lost in the operation of steam boilers and are the variable factors which have a direct effect on the percentage of heat imparted to the water in the generation of steam. In presenting certain data on these losses, illustrations of the origin, extent and methods which have been employed for their reduction, are submitted.

The loss which is generally the largest and in the majority of cases most easily reduced, is the heat carried away by the dry flue gases escaping from the boiler. Under this heading are included the sensible heat in the carbon dioxide and carbon monoxide, if any, formed by the combustion of the carbon in the fuel and the heat in the air in excess of that theoretically required leaving the boiler at the temperature of the escaping gases.

The principal causes of this loss are as follows:

(a) Improper methods of firing, which allow large quantities of air to enter the furnace either through the grates or fire doors.

(b) Condition of boiler settings. If the settings are cracked and the iron work is badly warped, a large amount of air is drawn through any openings, thereby reducing the draft available at the grate, diluting and cooling the gases as they pass over the heating surface.

(c) Poor quality of coal. Coals which contain a high percentage of ash or have a tendency to clinker cause an uneven distribution of the air through the fuel bed. When such a condition exists, large volumes of excess air enter the furnace and carry away heat in the flue gases. If the fuel is particularly fine, it will pack on the grate and produce an effect similar to that noted above.

This loss depends upon the weight of gases per pound of carbon burned together with the temperature at which these gases leave the boiler. The data which are required for this computation are the temperature of the flue gases, temperature of the boiler room, composition of the flue gases, the heating value of the coal and the carbon content of the fuel and ash pit refuse.

Several tests conducted in a plant in which the loss of heat in the flue gases was originally high are submitted in Table I. The plant in question consisted of hand-fired horizontal return tubular boilers equipped with plain grates upon which Pennsylvania semi-bituminous coal containing about 9.00 per cent of ash and 22.00 per cent of volatile matter was burned. The fires in this plant were carried at a thickness not exceeding 7 inches and were uneven, thereby permitting a very large air excess. The thickness of the fire

TABLE I—PLANT SHOWING EXCESSIVE LOSS DUE TO HEAT CARRIED AWAY BY DRY FLUE GASES LEAVING THE BOILER.

	Original conditions.	Tests to effect improvement in efficiency.	
1. Loss due to heat carried away by the dry flue gases	35.9	10.0	12.4
2. Loss due to evaporating and superheating moisture in coal and moisture formation of carbon monoxide	0.0	0.4	1.6
gen and distillation of oxyhydrogen compounds	2.7	2.7	2.8
3. Loss due to heat escaping through the formation of carbon monoxide	0.00	0.1	1.6
4. Loss due to combustible removed from the ash pits and from the grate during cleaning	3.2	7.6	4.5
Total determined losses	41.8	20.7	21.3
5. Loss due to unconsumed hydrogen and hydrocarbons, to radiation and unaccounted for (assumed constant for all tests)	8.9	8.9	8.9
6. Approximate percentage of heat absorbed by the boiler or boiler efficiency (by difference)	49.3	70.4	69.8
Total	100.0	100.0	100.0

*Paper presented at the Boston Meeting of the American Institute of Chemical Engineers, June 25-28, 1913.

†Fuel Engineer, Arthur D. Little, Inc., 93 Broad St., Boston.

was increased and the methods of firing were altered which resulted in a reduction of the loss of heat due to the enormous air excess from 36 to 12 per cent, with a resultant increase of about 20 per cent in the boiler efficiency. These tests afford conclusive evidence that the air excess maintained throughout the latter tests was somewhat lower than could be recommended for regular operation, as it will be observed that considerable carbon monoxide was formed under the existing conditions of air supply.

The loss of heat due to the incomplete combustion of carbon to carbon monoxide is usually an important factor in studying and perfecting the process of combustion. Carbon monoxide occurs in flue gases generally accompanied by tar vapors or particles of solid carbon in the form of smoke, together with small percentages of unburned hydrogen and hydrocarbon gases. The formation of carbon monoxide is due to the following causes:

(a) Furnaces of poor design.

(b) Improper methods of firing.

(c) The character of the fuel, particularly with reference to the equipment in which it is burned.

While the presence of carbon monoxide (CO) shows that some heat is lost through incomplete combustion, a small percentage of this constituent generally indicates that the air excess is reduced as low as practicable. A small amount of smoke, as evidence of the presence of carbon monoxide, is a more convincing indication of economical furnace operation than a smokeless stack which may be emitting several hundred per cent of excess air.

The extent of this loss is dependent upon the percentage of carbon monoxide (CO) and carbon dioxide (CO_2) as determined by the flue gas analysis, the heating value of the coal and the percentage of carbon in the coal fired and in the ash pit refuse.

The results of several tests in a plant where loss due to unburned gases, as indicated by the presence of carbon monoxide (CO), was particularly high, are shown in Table II. The boiler equipment consisted of hand-fired vertical tubular boilers having shaking grates. Coal from the Georges Creek field, containing approximately 18.00 per cent of volatile matter, was burned. The high loss due to incomplete combustion was not attributed to the character of the coal, although it had been proved that the furnace space in the boilers was not sufficient to burn coals containing higher percentages of volatile matter without the production of excessive amounts of smoke, indicating a large loss due to incomplete combustion. Aside from the question of furnace design, the primary cause of the high percentages of carbon monoxide (CO) was the thickness of the fires. By reducing the thickness from 30 inches to 12 inches and changing the manner in which the coal was fired, the loss due to this factor was reduced from 14 to 1 per cent, with a corresponding increase in boiler efficiency.

In the operation of a boiler plant, a certain percentage of the fuel which is fed to the furnace drops through the grate and is removed from the ash pit. An additional quantity of unburned coal is drawn from the grates in hand-fired plants when the fires are cleaned. The amount of fuel lost in this manner depends on:

(a) The character of the coal.

(b) The condition of the equipment.

(c) The methods employed in handling the fires.

If the coal is fine or non-caking and the grates contain large air spaces, excessive amounts of fuel drop into the ash pits. Certain coals clinker badly under some conditions of operation, and therefore during the removal of this clinker excessive amounts of unburned coal are drawn from the fires. Another cause of this loss is the frequent barring or raking of the fires when a fine or non-caking coal is used.

TABLE II—PLANT SHOWING EXCESSIVE LOSS DUE TO HEAT ESCAPING THROUGH THE FORMATION OF CARBON MONOXIDE (CO).

	Original conditions.	Tests to effect improvement in efficiency.	
1. Loss due to heat escaping through the formation of carbon monoxide (CO).	15.3	1.1	2.1
2. Loss due to evaporating and superheating moisture in coal and moisture formed by the combustion of hydrogen and distillation of oxyhydrogen compounds	4.1	3.8	4.2
3. Loss due to heat carried away by the dry flue gases	9.7	15.1	10.7
4. Loss due to combustible removed from the ash pits and from the grate during cleaning	3.2	3.5	3.3
Total determined losses	32.3	23.5	20.3
5. Loss due to unconsumed hydrogen and hydrocarbons, to radiation and unaccounted for (assumed constant for all tests)	11.2	11.2	11.2
6. Approximate percentage of heat absorbed by the boiler or boiler efficiency (by difference)	56.5	65.3	68.5
Total	100.0	100.0	100.0

The ash pit loss, which also includes the combustible removed during cleaning, is determined from the weight of this material, the percentage of combustible which is contains, together with the weight of the dry coal fired. For the purpose of this computation the heating value of the combustible is taken as 14,600 B.t.u. per pound. In special cases where complete boiler tests are not made and the weights of coal and ash pit refuse are not obtained, the percentage of the heat in the fuel removed with the ash pit refuse and cleanings can be computed from the analysis of this material and the determination of the percentage of ash in the coal as fired. In calculating this item by the latter method the assumption must be made that the percentage of ash obtained by the proximate analysis of the fuel represents the inert matter in the ash and refuse removed from the ash pits and the furnaces; that is, no account is taken of the ash which

is carried off the grates and deposited in the combustion chamber, upon the water heating surface or lost up the stack. A series of tests which indicate the extent to which this loss can be reduced are submitted in Table III. This plant was equipped with inclined grate stokers upon which Pittsburg slack coal was burned. The excessive rate at which the fuel was burned in order to maintain the required capacity caused deterioration of the grates, which allowed large amounts of unburned coal to fall into the ash pits. By careful attention to grate repairs and methods of operating the stokers the boiler efficiency was increased approximately 10 per cent.

TABLE III—PLANT SHOWING EXCESSIVE LOSS DUE TO COMBUSTIBLE REMOVED FROM ASH PITS AND FROM GRATES DURING CLEANING.

	Original conditions.	Tests to effect improvement in efficiency.	
1. Loss due to combustible removed from the ash pits and from the grate during cleaning	13.1	9.1	7.9
2. Loss due to evaporating and superheating moisture in coal and moisture formed by the combustion of hydrogen and distillation of oxyhydrogen compounds	3.2	3.3	3.4
3. Loss due to heat carried away by the dry flue gases	22.8	19.1	18.2
4. Loss due to heat escaping through the formation of carbon monoxide	0.0	0.0	0.0
Total determined losses	39.1	31.5	29.5
5. Loss due to unconsumed hydrogen and hydrocarbons, to radiation and unaccounted for (assumed constant for all tests)	7.5	7.5	7.5
6. Approximate percentage of heat absorbed by the boiler or boiler efficiency (by difference)	53.4	61.0	63.0
Total	100.0	100.0	100.0

The percentage of hydrogen in various coals is not an indication of their relative value when burned for the generation of steam. The essential feature in determining the effect of this constituent in the process of combustion is the form in which it is available in the furnace. Hydrogen, which is driven off in the uncombined state and burned by mixing with the oxygen from the air supply, is a valuable factor in the process of combustion, as it develops about four times the heat generated by an equal percentage of carbon. However, a certain percentage of the hydrogen in coal is distilled from the bituminous matter in the form of tar vapor and water. The nature of these compounds has been ascertained when coal is subjected to destructive distillation, as in the manufacture of illuminating gas, but the transformation through which this portion of the hydrogen passes in the boiler furnace is as yet undetermined. For the purpose of this discussion the theory of the code of the American Society of Mechanical Engineers for conducting steam boiler trials, for the loss due to hydrogen, is accepted. This theory assumes that all hydrogen contained in the fuel, together with an equivalent amount of oxygen in the form of water, is raised from boiler room temperature, evaporated in the furnace, and is eventually superheated to the temperature of the escaping gases. The amount of heat lost in this manner depends upon the composition of the fuel, the temperature of the boiler room and the temperature of the escaping gases. In addition to the loss due to evaporating and superheating the moisture formed by the combustion of hydrogen and by the distillation of oxyhydrogen compounds, a small loss is incurred by subjecting the moisture in the fuel and in the air used for combustion to these processes.

Increasing interest in the economical operation of boiler plants has resulted in marked improvement in efficiency in the majority of the plants where this matter has been given careful attention. An illustration of the distribution of heat in a boiler plant which was operating with high efficiency before tests were made for contemplated improvement is shown in Table IV. This plant consisted of large units of Climax water tube boilers equipped with circular grates which were fired through a number of doors. It will be noted from the tabulation that considerable loss due to the formation of carbon monoxide (CO) occurred, but this waste is more than counterbalanced by the particularly small percentage of combustible removed from the ash pits and furnaces. The amount of combustible in this material averaged about 12 to 15 per cent, representing a fuel loss of from 0.5 to 1.0 per cent. Although the operating conditions in this plant were excellent, still greater care in the methods of firing effected an increase in boiler efficiency.

TABLE IV—PLANT OPERATING WITH HIGH EFFICIENCY.

	Original conditions.	Tests to effect improvement in efficiency.	
1. Loss due to evaporating and superheating moisture in coal and moisture formed by the combustion of hydrogen and distillation of oxyhydrogen compounds	4.0	3.8	3.8
2. Loss due to heat carried away by the dry flue gases	14.4	10.1	11.8
3. Loss due to heat escaping through the formation of carbon monoxide	0.9	1.3	0.4
4. Loss due to combustible removed from the ash pits and from the grate during cleaning	0.6	0.8	0.9
Total determined losses	19.9	16.0	16.9
5. Loss due to unconsumed hydrogen and hydrocarbons, to radiation and unaccounted for (assumed constant for all tests)	8.0	8.0	8.0
6. Approximate percentage of heat absorbed by the boiler or boiler efficiency (by difference)	72.1	76.0	75.1
Total	100.0	100.0	100.0

Copper exports for September were 34,314 tons against 25,522 a year ago.

SULPHATE PULP FROM LONGLEAF PINE.*

By SYDNEY D. WELLS.

During 1912 the Forest Service in co-operation with the University of Wisconsin undertook a series of experiments on longleaf pine (*Pinus palustris*) with the following objects:

1. To study what influence the variable cooking conditions have in the sulphate process of pulpmaking.
2. To determine the suitability of longleaf pine for paper pulp.
3. To compare the sulphate process with the soda process.

This work has only been partly completed, but since there is urgent demand for information on the adaptability of longleaf pine, or southern pine, as it is more commonly called, for the manufacture of paper pulp, it has been thought advisable to give what indications our work has so far made manifest.

Longleaf pine was chosen on account of the large quantities of this wood that are being wasted in the lumber operations of the Southern States and also because many logs are at present being sawn into lumber at little or no profit on account of their small diameter which would be of admirable size for pulpwood. Furthermore, the large amount of resinous matter in this wood made it desirable as an extreme test of a cooking process and the long, thick-walled fibers of the wood assured a strong pulp if it could be produced without too drastic treatment.

COOKING CONDITIONS FOR FOUR-TYPICAL SEMI-COMMERCIAL COOKS.

	Caustic soda charged per 100 lb., bone dry chips.	Sodium sulphide charged per 100 dry chips.	Initial concentration of caustic soda in cooking liquor.	Initial volume of cooking liquor per 100 lb. bone dry chips.	Total duration of cook.	Duration at maximum steam pressure.	Maximum steam pressure.	Yield of crude pulp.	Beater Treatment. Duration of light brush.	Period of lowering roll.	Duration of stiff brush.	Per test per .001 of inch of thickness.
	Lb.	Lb.	Grammes per liter.	Gallons.	Hours.	Hours.	Lb. per sq. in.	Per cent.	Hours.	Hours.	Hours.	Lb.
Long yield	15.0	7.5	26.5	.68	3.0	2.8	90	61.2	1.5	.5	2.0	7.0
Medium yield	15.0	7.5	26.5	.68	3.5	3.0	100	49.0	4.0	.5	2.5	9.0
Small yield	20.0	10.0	44.6	.54	3.0	2.5	103	45.3	1.5	.5	1.5	10.0
Soda cook	30.0	0.0	90.0	.40	6.0	5.5	100	39.8	6.0	.0	.0	9.0

EXPERIMENTAL PROCEDURE.

The cooking operations in this work were conducted in two forms of digesters. The first form consisted of a small rotary autoclave of about 2-gallon capacity which was heated with Bunsen burners. The other form was a vertical digester, of 60-gallon capacity heated by direct steam. The greater portion of the work was accomplished in the former and in all 145 cooks were made. The data obtained in these cooks were used in determining the conditions to use in the larger digester in which nineteen cooks were made to obtain conditions more nearly comparable with those obtained in commercial practice.

The wood used was procured in Louisiana and Mississippi, and was fairly average in rate of growth, size, and content of resinous matter. It was freed from bark and reduced to chips of five-eighth-inch long with the grain. These chips were allowed to become air-dry and were thoroughly mixed and sifted to remove any dirt and small pieces.

The cooking liquors were made up by dissolving the required amounts of commercial caustic soda, sodium sulphide, Glauber's salt and soda ash to produce solutions of the desired concentration of each of these chemicals.

In studying the influence of the variable factors entering into the cooking operation the small autoclave was used. The effect that any one variable condition exerted was determined by a series of cooks made varying the condition under observation, and maintaining the other conditions as nearly identical as possible in each cook. The effect of the results were ascertained by determining the yield of pulp and carefully treating the pulp in a hollander beating engine to develop a stuff capable of producing as strong a sheet as possible when made into paper. The quality and color of the pulps were judged by inspection, feel, amount of beater treatment necessary, and the strength and wearing qualities of the paper produced.

THE EFFECTS OF VARYING THE AMOUNTS OF CHEMICALS.

The effect of varying the caustic soda or sodium sulphide was a decrease in yield and a lighter colored pulp with an increase in either one or both of the chemicals. Caustic soda was found to be about twice as drastic in its action as sodium sulphide, and with the same yield the pulp produced by the former was lighter than that produced by the latter. The yields, however, do not decrease directly in proportion to the amounts of chemicals used, and between 30 and 50 lbs. of caustic per 100 lbs. of chips the decrease in yield is much less for equal steps than below or above these amounts. The disagreeable odor caused by the production of mercaptans increased with the increase of the sodium sulphide, and was much more noticeable where the larger proportions of this chemical were used.

*Paper read before the Rochester Section of the American Chemical Society, Sept. 10, 1913.

The sodium carbonate and sulphate present in the cooking liquor produced no very apparent effect except where the former was present in relatively large amounts, when a retardation in the action of the other chemicals present was noticeable. Enough cooks were not made, however, to definitely establish this indication.

The Effect of Varying the Pressure, Duration of Cooking and Concentrations.—The effect of increasing any one of these variables was to increase the severity of the cooking action attainable with the same quantity of cooking chemicals. With any combination of the above conditions there is a definite amount of chemical necessary to produce a pulp of the best quality, and it is possible to use a wide range of conditions to produce approximately the same result.

Semi-Commercial Cooks.—In the cooks in the large digester the object sought was to obtain the best quality of pulp. It was found that easily-bleaching pulps could not be obtained without using a very drastic digestion with a high percentage of alkali, and that the pulps produced were very low in yield and extremely soft and weak. It was, therefore, decided to devote attention toward producing the strongest pulps possible, and treat these pulps in the beater to make the highest grade of "kraft." Although the strength of the paper was constantly considered, the question of yield was also very important, and the best books were determined with these two objects in view.

An average sheet of .005 of an inch tested 45 lbs. and weighed 45 lbs. per ream of 500 sheets 24 in. by 36 in. Not only was the paper exceptionally strong but it was very resistant to wear and folding. The latter fact is apparent by some tests made on it in a Schopper folding tester in which it withstood 1,200 double folds before breaking.

The pulps produced under these conditions were very chippy when blown but the chips were very soft, had no hard hearts and were readily broken up in the beater. An ordinary hollander with steel fly bars was used and the pulp was beaten two hours at light brush, four hours at stiff brush, and half an hour was spent in lowering the roll from one stage to the other.

Stronger paper than these were produced but the yields fell off considerably. Yields up to 61 per cent were obtained but the strength fell off more than could be compensated by using proportionately heavier paper.

Soda Cooks.—To compare the soda process with the sulphate process in cooking longleaf pine several soda cooks were made. It was found that soda pulps could be made that would produce paper capable of resisting bursting pressure to the same degree as the best paper made from sulphate pulp, but the wearing qualities were not nearly as good and the yields were from 5 to 10 per cent less. The unbeaten pulps were soft and fluffy for even slightly undercooked pulps, and although they could be hardened in the beater, the treatment was longer and much greater care had to be exercised to avoid cutting the fibers. Furthermore, although a fairly good grade of kraft can be made of sulphate pulp with a yield of 60 per cent soda, pulp produced with that yield would be so undercooked and brittle that only very poor wrapping could be produced. Moreover, it was found necessary to cook soda pulp at least six hours to secure good results, while in the sulphate process three and one-half hours were found sufficient. Thus in the latter process the same digester capacity would produce two-thirds more pulp a day.

General Conclusions.—Although the experiments performed in this investigation are only a portion of what are contemplated, they seem to make apparent the following facts:

1. That longleaf pine is well adapted for the manufacture of natural-color kraft pulps and papers.

2. That the sulphate process when applied to this wood affords pulps of better quality and higher yields than the soda process.

3. That kraft paper can be made from longleaf pine equal or superior in quality to the imported or domestic kraft papers now procurable.

4. The high specific gravity of the wood insures a greater yield per cord to this wood than is possessed by any other commercially important pulpwood.

The following table gives the amount invested by new companies in German textile undertakings, and the capital increases made by existing firms during the period January to August for some years back:

Year.	New undertakings.		Capital increases.	
	Companies.	Capital.	Companies.	New capital.
1907	20	$2,975,000	8	$1,904,000
1908	28	2,737,000	12	1,238,000
1909	41	3,284,000	12	1,095,000
1910	33	4,332,000	13	997,000
1911	29	2,428,000	16	1,475,000
1912	35	3,570,000	9	547,000
1913	38	4,831,000	24	2,380,000

The average rate of dividend paid by most branches of the industry shows a marked advance compared with last year. During the period January-August, 1913, the average rate of dividend paid by 216 textile companies, representing an aggregate capital of $98,341,000, works out at 8.6 per cent, against 7.1 per cent last year. The following table gives the particulars for the various branches:

	Companies.	Capital in 1911-12.	Capital in 1912-13.	Dividend. 1911-'12. Pct.	Dividend. 1912-'13. Pct.
Cotton spinning	25	$ 9,020,000	$ 9,115,000	5.3	8.7
Cotton weaving	12	3,760,000	3,737,000	6.9	9.4
Spinning and weaving	32	16,374,000	16,136,000	3.6	6.8
Worsted spinning	27	14,685,000	14,685,000	8.0	8.0
Woolen manufacturing	29	19,088,000	19,111,000	8.1	8.5
Linen and jute spinn'g	24	11,091,000	11,234,000	6.7	9.0
Silk weaving	6	2,785,000	2,523,000	5.2	4.2
Other manufacturing	47	18,493,000	18,516,000	10.3	11.8
Dyeing, finishing, etc.	14	3,213,000	3,284,000	3.4	4.5

During the first seven months of the present year there was exported from the Federated Malay States 12,265 tons of cultivated rubber, against 8,071 tons during the similar period of 1912. The value of the exported rubber was $21,022,746, upon which the Federated Malay States have collected a duty of $524,567.

METHODS OF TREATING PAPER MILL WASTES.*

By EDWARD HUTCHINS.

At the present time very little is known about the purification of trade wastes, and this is especially true of paper mill wastes. In the writer's opinion, there will be developed, in the near future, much better methods of treating suspended matter than those now in general use, and ways will be found to treat successfully waste boiling liquors which have not been economically disposed of.

The subject of trade wastes is made more difficult by the fact that there are no set standards of purification which can be used as guides by engineers engaged in disposal work. It would simplify the whole problem if it were known, in advance, what amount of purification would be required. No matter how much the manufacturer may be in accord with the idea of a clean river, he does not feel justified in spending any more for disposal works than is necessary to satisfy the public, and he is entirely justified in this attitude. In fact, he is obliged to take this stand because his competitors, being better situated for the time being, do not have to purify their wastes, and thus have him at a disadvantage.

With the present uncertainty as to what will be required, the manufacturer usually directs the engineer to spend as little money as possible in getting him out of his difficulty. Thus the most important question the engineer has to solve is the personal equation of those charged with the enforcement of the law. In nine cases out of ten, this results in a plant that may be acceptable for a year or so, but which will not permanently or satisfactorily dispose of the wastes. In this way money is wasted that would have been expended to better advantage had it been known what was required.

It should be the duty of authorities, charged with the purification of rivers, to formulate definite requirements and to inform the manufacturer of the degree of purification required. With this information, the manufacturer can ascertain what disposal works will cost and determine whether he can afford to stay on the stream or not.

If, as the Massachusetts Drainage Commission states, we are to plan to have pure rivers, then the legislature should define what is meant by a pure river and adopt the standards to which all rivers, now pure, must be kept and to which rivers now polluted shall be brought by progressive stages, these stages to be fixed by the State board of health, or similar body. Thus at the end of a fixed term of years off rivers would be clean and the manufacturer would have distributed the burden over a term of years.

The standard should be a practical one, commercially attainable, which would allow manufacturers to utilize the rivers in the disposal of their wastes so long as the wastes do not pollute the rivers beyond the point where fish can live in the water and the rivers be pleasant for recreative purposes. Two standards might be required, one for the streams used as public water supplies and another for streams used for manufacturing purposes. We are only concerned with the latter.

Standards of this kind would change the attitude of the manufacturer from one of procrastination and half measures to one of action. He would desire to get what must be done, done and out of the way. He would not ask the engineer how little he could do and escape prosecution, but would instruct him to build a plant to treat his wastes so as to meet the standards, and to keep the expense as low as possible.

The writer knows that such standards are hard to formulate, but there is no reason why it cannot be done, and as a matter of fact such standards have been proposed from time to time. Let the State board of health ask the legislature to appoint a commission to investigate the situation and devise these standards. Then let the legislature adopt them, and a long step in the right direction will have been made. A similar action to that proposed was taken in the case of railroad grade crossings, and it has produced satisfactory results without too great a burden on anyone.

The State board of health should be charged with the enforcement of the standards. They should see that the river waters of the State are brought to the standards as quickly as is consistent with fairness to the manufacturers and that as few of them as possible are forced out of the State. Rivers now polluted should be studied and the State board of health should make a set of progressive standards for each river. After these have been adopted, the State board of health should notify the interested manufacturers that on such and such dates they would be expected to have reached certain stages in the purification of their wastes, the amount of purification to be judged by the condition of the river water below their plants. In this way the standard for these rivers can be gradually raised without asking more of the manufacturer than is reasonable, and without going beyond the known possibilities of the art of waste disposal. The manufacturer will be able to spread his expense over a term of years and the public will know that the rivers will finally be in a satisfactory condition.

WASTES TO BE HANDLED.

The manufacture of paper is not carried on in the same manner for any two grades, but the processes are similar and the variations usually consist in omitting one or more of the stages to be mentioned.

The raw material, wood, paper, rags or other stock, is first cut into small pieces and dusted. These operations produce the "solid wastes." The stock is then boiled in an alkaline or acid solution to break down the fiber and to remove grease, dirt, resins, etc. The spent

*From Paper.

liquors from this boiling produce the "boiler wastes."

The stock is next washed to remove the chemicals and loosened dirt. It is then bleached and again washed to remove the spent bleaching fluid.

The water used in these two operations is called "wash water" and the wastes "washer wastes." They are usually similar to the boiler wastes in composition, except that they are diluted. Washing is usually done in large tubs, in which the stock is circulated. The dirty water is removed continually by means of a revolving wire-covered cylinder, fitted with buckets on the inside. Fresh water is added as fast as the dirty water is removed. The washing is often done in the beating engine. After the washing, and in many cases during the washing, the stock is beaten—that is, reduced by mechanical means—to the proper length and condition for the formation of paper. Beating is a cutting, drawing or bruising process, or a combination of all three, depending on the quality of product desired. When the beating is complete the stock has been reduced to pulp and is ready for the manufacture of paper. This stock is then further diluted with water and pumped to the paper machine, where it is formed into sheets by one of two processes. The first is by means of wire-covered cylinders revolving in fine vats of dilute stock. The water passes through the wire cover and the stock is retained on its surface, from which it is removed in a continuous sheet. The second is by means of a horizontal wire cloth belt conveyor, made of fine mesh wire, one end of which receives the dilute stock and carries it forward. The water runs through the wire while the stock is retained on its surface.

In either case the stock is removed from the wire cloth to a woolen carrier belt, called a "felt," which takes it through a series of presses and delivers it in the form of a partially dried sheet to the driers. From the driers it is carried to the calendars, slitter and winder, where it becomes the finished product. The paper is called cylinder machine paper or Fourdrinier machine paper, depending on the type of machine on which it is made.

In the process of forming paper, large quantities of water are used, but fortunately most of this is used over and over again. A certain amount of fresh water has to be added to clean the felts and wires and to prevent an accumulation of slime and dirt. This added water requires the withdrawal of an equal amount of waste water to keep the vats from overflowing, and this water is known as "machine wastes."

Hence the wastes to be disposed of are of four classes—solid, boiler, washer and machine wastes. These will be discussed separately and an idea given of the amount and character of the wastes.

Solid Wastes.—The disposal of the solid wastes does not ordinarily cause trouble, as they can be burned as fuel. These wastes vary in amount from nothing in some mills to as high as 20 per cent of the original stock. The dustings from fibrous material, which may amount to 3 or 4 per cent of the stock and consist of short fibers, dirt, etc., have in some mills been used in connection with liquid wastes as fertilizer. Slivers and like matter from wood mills have been allowed to go to waste, but they are readily saved and either made into pulp or burned with bark and other refuse.

Boiler Wastes.—Many mills do not boil their stock, but those that do are considered under three classes, depending on the treatemnt given the stock. These are rag mills, sulphite mills, soda and sulphate mills. Under the term "rag mill" will be included all mills that use old material such as rags, rope, burlap, old papers and the like, not requiring too drastic treatment of the stock to render it fit for paper making. Stocks of this kind are usually boiled in long horizontal boilers, revolving slowly under a pressure of 20 to 30 lbs. of live steam. They are boiled in a solution of lime or caustic soda, or a mixture of both, for several hours, after which the spent liquor is blown off and the boiler emptied.

The amount of waste liquor to the ton of stock varies greatly and depends on two things: first, on the amount of liquor used in boiling; and, second, on the care with which the liquor is drained away from the boiled stock. It varies from 100 gal. to perhaps 300 gal. per ton of stock and may be said to average about 150 gal.

The quality of the waste liquor varies with the chemicals used and with the stock. As a rule, it is very strongly alkaline and is very badly polluted with dirt, alkaline soaps, etc. Much of the foreign matter is in solution and much of the matter in suspension is in such a fine state that it will not settle even when using a reasonable amount of coagulant. Filtration will remove only the matter in suspension. There can be no bacterial action due to the strong alkali. Filtration is also difficult from the tendency of fine material to clog the filters. The only way that they have been treated, so far as the writer knows, is by evaporation. Where large amounts of caustic soda are used, the recovery of this by evaporation might make a satisfactory method of treatment, but there are several conditions which make it much less profitable than in the soda process mills to be described later. In the first place the amount of organic matter in the waste is comparatively small, due to the less severe boiling of the stock, and hence more fuel is required to evaporate the liquor; second, the amount of caustic used is less per ton of product and more wash water is required to remove the dirt; lastly, with the usual small amount of liquor to be treated the apparatus and labor costs are so great that recovery is out of the question. A method of evaporation which has been suggested is to place the wastes out of doors in shallow pools, where they can be evaporated by natural heat. This should make a satisfactory method of disposal for small quanties. Another method is to use them for sprinkling the streets. Where the public will allow this method,

it is very satisfactory. The soaps and gums in the waste seem to have the property of cementing the fine dust particles and, in this respect, to act similarly to road oil. The effect, however, does not last as long. Another method of treatment is to combine evaporation and filtration by applying the waste to land so situated that the liquid will partially evaporate and partially filter back to the water course, being diluted on its way by the ground waters. Large areas are required for this purpose, and in time they become clogged so as to be useless for filtration.

It has been suggested that these boiler wastes be used as a fertilizer, and this will be well worth looking into, where other means of disposal do not look promising.

The following analysis shows that in some mills there is a large amount of nitrogen which should be valuable.

ANALYSIS OF BOILER WASTES, RAG MILL.

Parts per 1,000,000.

Nitrogen	297.3
Potash	0.
Phosphates	0.
Alkali	9,370.

By adding phosphates and the dustings from the rags, this might be made into a fertilizer which would allow the waste to be disposed of without too great expense.

Sulphite Mill Wastes.—The sulphite process is used in the reduction of wood exclusively, and is carried out as follows: The wood is barked and cut into small chips. The chips are fed into large stationary or rotary boilers called digesters. The bisulphite liquor, made by absorbing sulphur dioxide gas in a solution of milk of lime, is then added to the digester and steam turned on. The mass is cooked for about eight hours, under 80 to 90 lbs. of steam. The whole charge is then blown into a pit with a perforated bottom called a blow pit. The waste liquor drains away and runs to waste. There is a loss of 250 to 350 lbs. of sulphur and about 50 per cent of the weight of the wood per ton of pulp made. In "Wood Pulp," by Cross, Bevan and Sindall, there is a good resume of the present state of the art of sulphite liquor disposal. They state that there have been many attempts to recover the sulphur or other by-products, but that no system has yet been introduced for the recovery of the wastes, on a commercial scale, which is likely to be remunerative.

They give nearly a complete list of the patents and suggestions that have been advanced. Many of these produce by-products of some value, but have nearly as bad wastes remaining to be treated as the original liquor.

Among the by-products proposed are: Tanning agents; size for paper and textiles; glue for various purposes, including glue for briquetting fuel; mordant for woolen goods; colors; soap; fertilizers, alcohol, etc.

Hoffman gives the analysis of several sulphite waste liquors as follows:

ANALYSIS OF SULPHITE PULP WASTE LIQUORS.

Grammes per liter.

	(1)	(2)	(3)	(4)	(5)
Total solids	82.0	88.0	85.0	93.0	92.0
Loss ignition	68.0	75.0	69.0	81.0	...
Ash	14.0	13.0	16.0	12.0	...
Total sulphur	...	...	...	...	9.2
Free sulphur dioxide	2.6	2.2	2.9	2.6	3.8
Sulphide radicle (SO)	7.3	7.9	6.7	1.2	3.8
Sulphate radicle (SO)	4.1	5.4	4.8	2.7	1.9
Oxygen consumed	52.0	52.0	50.0	60.0	...

Soda Mill Wastes.—The soda process is used in the reduction of wood, straw and other fibers, and is similar to the sulphite process, except in details and in that the reducing agent is caustic soda. Caustic soda is so valuable, and such large quantities are necessary to reduce the fiber, that it is always recovered. Hence these wastes do not pollute the rivers. This is fortunate, as a worse liquor would be hard to find.

In making soda pulp, the wood is prepared as for sulphite, and then put in boilers with 16 to 20 per cent of custic soda, based on the weight of the wood. The boiler is a rotary or stationary boiler and the pulp is cooked under 70 to 80 lbs. of steam for eight or nine hours. It is then emptied into drainers and the waste liquor drained and washed out. The wash water is kept as low as possible in this process and is treated in connection with the boiler wastes. The limit of wash water and boiler wastes for economical operations is about 1,000 gal. a ton. The combined liquors are evaporated to a thick syrup and finally burned to "black ash," which is an impure carbonate of soda. This is made into caustic soda in the usual way by boiling up with quicklime. The clear liquor thus formed is used for the reduction of more wood. The loss of soda in the cycle is about 20 per cent.

This waste can be economically treated because it contains at least 50 per cent of the original wood in solution and this organic matter supplies most of the fuel needed to effect the evaporation. The evaporation of the weak liquors in this country is done in a multiple effect evaporator and in England by a multiple effect or a Porian evaporator. The thick liquors are burned in a furnace, the heat from the furnace being used to help evaporate the weak liquors.

The successful operation of the plant depends, to a great extent, on the care with which the evaporation, as a heat-consuming operation, is conducted, and the care with which the wash water is regulated.

Sulphite Mill Waters.—This process is used in the reduction of wood and is similar to the soda process, except that the caustic soda is made from the sulphate of soda, instead of from carbonate. There are also other slight differences. Vile odors are produced in the course of the process, and hence it can be used only in sparsely settled communities. The waste liquors are always recovered and there should be no stream pollution. The recovery process is similar to that used in soda mills.

METHODS OF ANALYSIS USED IN THE LABORATORIES OF THE ARMOUR INSTITUTE OF TECHNOLOGY.

The Milling of Wheat and the Testing of Flour.

THE BAKING TEST.

The baking test has for its object the grading of flour upon the basis of its actual performance in the baking of bread. To this end, the following observations are made and expressed numerically:

(1) Absorption of water by flour.
(2) Color of loaf.
(3) Loaves per barrel.
(4) Size of loaf.
(5) Quality of loaf.
(6) Fermenting period.
(7) Quality of gluten.
(8) Average value.

The test consists in the baking of loaves from the flours to be graded, together with two loaves made from the laboratory's standard flour. Of the above tests all but the first are expressed in percentage figures, the standard being taken as 100 per cent. The "average value" is the average of all the percentage figures.

METHOD.

A modification of the baking tests as outlined in Bulletin 117 of the Kansas State Agricultural College was used, because several things were thought necessary to bring the test into such form that its results would more closely give the actual commercial value of the flour.

In making baking tests on different flours it is above all desirable that the test should be so conducted that the differences in the results should be caused by the inherent qualities of the flour and not by variations due to the method employed. However, in practice the skilled baker adapts his method to suit the different flours he uses, and he remedies the defects in the flour to some extent by the method of baking he uses. Therefore it has been the writer's aim to conduct these tests in such a way as to get as good bread as possible from the different flours, and if necessary to vary the method of baking in some slight details to be able to do this. That such a method will yield results that more closely approximate the results the flour is going to give in actual use is apparent.

The actual baking and its associated tests were made as follows:

The Straight Dough Test.—In these tests "dough" means a flour mixture that has been subjected to a short period of fermentation and baked as soon as the dough has risen a standard amount. This amount is fixed by preliminary trial and is uniform in all these tests. The short period of fermentation varies from 1 to 3 hours and is secured by using fresh yeast in large quantities.

Before making the dough we must know the percentage of water that the flour will absorb to be of correct stiffness. This is found by weighing out 30 grams of the flour into a strong teacup and running in distilled water from a burette until the resultant dough is "right." The best test that the dough is "right" is to put it on the bottom of the cup in the form of a round ball and watch it for about 3 minutes. If it gradually settles down until it touches the rim of the circle on the bottom of the cup it is satisfactory. If it stays in the original shape it is too stiff, whereas if it quickly subsides and overlaps the edge of the cup it is too thin. This test will be found to be sensitive in careful hands to within 25 c.c. on 30 grams of flour. The water that the flour absorbs is figured in percentage.

Now the dough can be made: 340 grams of flour, 10 grams of sugar, and 5 grams of salt are weighed out. The amount of water as determined by the absorption test, less 50 c.c., is also measured out. The flour is placed in the pan it is to be baked in and placed in the constant temperature oven until it reaches 35° C. As many grams of yeast as are necessary for the whole batch of loaves are weighed out and dissolved in enough cold water to just be able to draw out 50 c.c. of the resultant solution for each batch of dough. 10 grams of yeast should in this way get into each batch of dough.

When the flour is warmed to the right temperature it is removed from the oven and two-thirds of it is placed in a dish. The water as measured out is heated to 42° C. and the sugar and salt dissolved in it. Then exactly 50 c.c. of the yeast solution are withdrawn in a pipette and added to the sugar and salt solution. The temperature of the resulting mixture should be very close to 35° C. This liquid mixture is then added to the flour. The resultant batter is beaten up with a large spoon or spatula until there are no more lumps, which usually takes about 2 minutes. The remainder of the flour is then added and the dough mixed, first by means of spatulas and then the hands, to a ball of well kneaded consistency. After this operation, which usually takes but two or three minutes, the dough is placed back in its pan, which has been buttered in the meantime, and put back in the rising oven where it is

kept at 35° C. The dough is weighed at this juncture to ascertain the loss during the kneading. This loss is unavoidable, and usually is about 15 grams. It is due mostly to evaporation of moisture and sticking of some flour to the hands.

The dough is now allowed to rise the standard amount and if it is a *very* weak flour from a soft wheat, it is immediately baked, but if the flour has any reasonable strength it is knocked down, rekneaded, and allowed to rise a second time, and at the termination of this rise if the dough of one of the loaves shows signs of collapsing that loaf is then baked, otherwise a third rise is used. Most flours coming from sound wheats will stand three rises; they will even need them. The times of rising are carefully noted, and all loaves are baked exactly 30 minutes at 238° C. About ½ to ¾ of an hour after the loaf has been standing in the open air, it is weighed, and this weight is recorded as the weight of the hot loaf. This must of course be kneading.
corrected for the small amount of dough lost in the

In measuring the volume of the loaf it is put in an oblong box that already contains some turnip seed. Then the box is filled with the seed, gently rapped, and the seed leveled off at the top. The seed is poured out and weighed, and from the weight of seed that the box will contain when there is nothing but seed in it, the volume of the loaf can be obtained, since the volume of the box is known. This method has been found to be accurate to within 5 grams of seed, which corresponds to about 2/5 cu. in. in volume.

The volume should be measured approximately one hour after removing the loaf from the oven as it will shrink more and more the longer it stands.

Gluten Expansion Dough Test.—This is for the purpose of testing the quality of the gluten and checking the relative fermentation period of the flour. The proceedure is identical as for the straight dough except that 100 grams of flour are used instead of 340 grams, and the other ingredients in proportionate amounts. At the point where the regular dough would be panned, this dough is placed in the bottom of a well greased glass cylinder which is at a temperature of 35° C. and placed in the rising oven at 35° C.

For the first hour no attention is required, but after that the height of the dough and the time should be recorded every 15 minutes; and later when it is evident the dough is near its maximum volume, every five minutes. When the dough just begins to fall the volume and time are noted. From the difference in initial and final volumes the relative qualities of the glutens are calculated. Since we start with the same amount of flour, the quality of the gluten itself will be equal to the net rise divided by the per cent gluten in the sample. This figure is then referred to the similar figure of the standard flour on a percentage basis.

Another method of performing this test which seems to yield more definite results uses the gluten itself instead of the dough. For this purpose the gluten is washed out of the flour in the usual way, and then 10 grams of each gluten is placed, wet, in a tin cylinder 1 inch in diameter and placed in the bake oven at 200° C. It will be found that the gluten will expand and after twenty-five minutes will have formed a porous column within the tin. The height of this column will be directly proportional to the quality of the gluten.

In making all these tests, a flour the baking qualities of which are known, is selected and tested at the same time as the other flour. The results are compared on a percentage basis and in this way the unknown flour is judged.

We are led from our laboratory experience to make the suggestion that some form of mechanical kneeding apparatus which can be kept at constant temperature should be used in all of the kneeding operations. If this is not done, there is considerable chance for variation in the results obtained for fermenting period, texture and size of loaf. We also suggest that the color be determined on the samples of flour rather than on the bread and that this color be determined with such an instrument such as the Lovibond tintometer and that it be expressed in the number of standard color used rather than by any percentage system which may be based on the standard flour. At present there seems to be a different method of expressing color in use by each laboratory engaged in flour testing.

We may sum up the results we have been able to obtain in our experimental work on the milling of wheat and testing of flour by saying that we are able to secure results which are satisfactory to us in showing the flour producing qualities of any wheat. We will qualify this statement by saying that, at the present time, it is very difficult to express our results in such a way that they will convey an adequate understanding of these results to other parties such as millers or flour jobbers.

Iron ore shipments from Imataca, Venezuela, to Philadelphia, Pa., are steadily increasing. Seven vessels are now under charter, and shipments for September totaled about 11,000 tons, while October shipments are expected to reach 15,000 tons, and by the end of the year 30,000 tons monthly.

The Federation of Princeton Clubs of New Jersey has completed plans which are expected to result in the foundation of a $100,000 chair in engineering chemistry for Princeton University. A committee of 26 has been drawn from the Jersey alumni to receive funds. The committee is divided into two sections—one section for a canvass of the Princeton University alumni in New Jersey and the other for a canvass of the manufacturers of the state.

KUKUI (CANDLE-NUT) OIL.*

By ALICE R. THOMPSON.

Kukui oil, commonly known as candle nut oil, is extracted from the nut of the Kukui tree (*Aleurites triloba* or *A. moluccana*). The tree is generally distributed through Polynesia, Malaysia, Philippines, Society Islands, India, Java, Australia, Ceylon, Bengal, Assam, China, Tahiti, and Hawaii. In Hawaii, Kukui is found growing on all the islands in the lower mountain zone. As the oil is of considerable commercial value, investigations were made on the nuts and oil of samples sent to this station.

The oil commonly known as candle nut oil belongs to the class of drying oils, valuable therefore as a paint and varnish oil. It is also used for soap-making and is a good illuminating oil. It is produced in large quantities in Australia, China, New Zealand and the Fiji Islands,[1] and is exported to America and Europe in ever-increasing shipments.

When extracted from the crushed kernel by ether or petroleum, the oil is light yellow in color, with a specific gravity of 0.92. When expressed, the oil may be dark colored, due to impurities. It dries in thin films on standing several days.

At this station, a sample of oil was extracted by gasoline from the crushed kernels, the gasoline removed by evaporation and an analysis made on the oil to determine its chemical and physical properties. The values are as follows:

Specific gravity	0.92 at 15.5° C.
Saponification value	179.1
Iodine number	155.5
Hehner value	89.9
Soluble acids	1.71
Reichert-Meissl number	2.82

The fatty acids congealed to a pasty mass between 18° and 20° C. The oil itself was still fluid at — 3° C. Fendler[2] found the congealing point of candle nut oil to be — 15° C. The oil was soluble in ether and slightly soluble in alcohol. Concentrated sulfuric acid colored it dark brown.

The drying property of the oil is indicated by the high iodine value. Linseed oil, which is a fine drying oil, has an iodine value of 170-181.[3]

A sample of oil expressed from kukui nut was sent by Mr. Anderson to this laboratory. The oil was in a crude state, containing suspended matter, and had a dark red color. The oil had the following values:

Specific gravity	0.92 at 15.5° C.
Saponification value	190.2
Iodine number	164.2

In the following table are given the values found by chemists in the oil of *Aleurites moluccana* obtained in other parts of the world:

	(1)	(2)	(3)	(4)	(5)
Specific gravity at 15° C.	0.925	0.920–0.926	0.925	0.925	0.924
Acid value	1.72	.....	.....	0.97	0.5
Saponification value	204.2	184 –187.4	192.6	194.8	189.5
Iodine value	139.7	136.3 –139.3	163.7	114.2	152.8
Hehner value	96.4	.....	95.5	.....	95.2
Volatile acids	1.98	.....	.....	1.2	.....
Titer	17.8	.....	.....	.....	.....
Butyro refractometer	.....	76-75.5(15°C.)	76(25°C.)	.....	.....

(1) Imperial Institute, *Bull. Imp. Inst.*, 5, 135-136 (1907); (2) De Negri, *J. Soc. Chem. Ind.*, 20, 909 (1901); (3) Lewkowitsch, *Ibid.*, 20, 909 (1901); (4) G. Fendler, *Ibid.*, 23, 613 (1904); (5) Kassler, *Ibid.*, 22, 639 (1903).

The values vary to some extent in these analyses; nevertheless, the general characteristic of high iodine value and saponification extends throughout.

CONSTITUENTS OF THE KUKUI KERNEL.

Several samples of nuts were obtained and the fat especially determined in the kernels. The fat content appears to vary but a few per cent in the kernels of nuts a year old or fresh. The fresh nuts naturally contain more moisture.

	1-year-old nuts, per cent.	Fresh nuts, per cent.	Immature nuts, per cent.
Moisture	3.55	7.14	13.39
Fat	65.00	66.25	56.7
Ash	3.56	3.05	....
Protein	18.75	19.88	....
Fiber	2.14	1.39	....
Nitrogen-free extract by difference	7.00	2.29	....
	100.00	100.00	

The fiber and the ash are very low, the principal constituents being fat and protein. It is of interest to note in this oil-seed the small percentage of hydrolyzable carbohydrates (only 1.40 per cent by analysis). A qualitative test showed the absence of starch in the kernels. The quantity of fat, if calculated to the water-free basis, is quite constant in the three samples.

Analyses made of the kernels of this same nut, *Aleurites moluccana*, by various chemists are given in the table below:

	(1) Per cent.	(2) Per cent.
Water	5.00	8.25
Oil	62.175	59.93
Protein	22.653	8.04
Nitrogen-free extract	6.827	17.62
Ash	3.345	3.56
Fiber	.....	2.62
	100.00	100.00

(1) H. Semler, *Die Tropische Agrikultur*, 2, 515; (2) N. S. Wales, *Agri. Gazette*, 17, 859 (1906).

The mineral constituents of the kernel were also determined in this laboratory, as shown in the following table:

	Per cent.
Mn_3O_4	0.03
CaO	0.17
MgO	0.60
P_2O_5	1.59
K_2O	0.75

On extraction of the oil these constituents[4] increase in proportion to the dry matter. The residue contains,

*From the Journal of Industrial and Engineering Chemistry; abstracted from Press Bull., 39, Hawaii Experiment Station, U. S. Department of Agriculture.

[1]Bull. Imp. Inst., 5, 135, 136 (1907).

[2]J. Soc. Chem. Ind., 23, 613 (1907).

[3]"Commercial Org. Analysis," Allen, Vol. II, Pt. I, p. 97.

[4]Bull. Imp. Inst., loc. cit.

[5]Agr. Gaz. N. S. W., 17, 859 (1906).

[6]Agri. Gas. N. S. W., 17, 859 (1906).

therefore, large amounts of phosphoric acid, potash and nitrogen, all valuable as fertilizing ingredients. Analysis of the residue of ground up kernels extracted with ether for two days is as follows:

	Per cent.
Moisture	2.42
P_2O_5	2.79
K_2O	2.77
Protein	53.75

Press cake obtained commercially by expressing the oil from kukui nuts would compare favorably with the residue, as most of the oil can be expressed. According to an article in the *Agricultural Gazette*,[5] 55 per cent oil can be obtained from kernels containing 60 per cent. Analyses of press cake made elsewhere show it to be valuable as a fertilizer.

ANALYSIS OF PRESS CAKE.

	(1) Per cent.	(2) Per cent.
Oil	8.8	5.5
Moisture	10.00	10.25
Ash	8.28	....
Protein	46.16	47.81
Fiber	1.47	....
P_2O_5	1.39	3.68
K_2O	1.95	1.53
Mg and Ca	....	7.19

(1) Lewkowitsch, *J. Soc. Chem. Ind.*, 20, 909 (1901); (2) H. Semler, *Die Tropische Agrik.*, 2, 515.

Press cake cannot be used as a fodder in spite of its apparent food value, as it has a poisonous effect upon stock.[6]

The proportions of fat to kernel and whole nut were determined in several samples. In a sample one year old in which the fleshy husk that covers the shell when the nut is green had decayed away, the kernel weighed 31.5 per cent of the hard nut. As the fat content of the kernel was 65 per cent, the fat content of the nut minus the husk averaged about 20 per cent.

In a sample of fresh nuts, the kernel was 29.3 per cent of the nut minus the husk and 12.1 per cent of the nut with the husk on. The fat content of the kernel was about 66 per cent. It was, therefore, about 8 per cent of the nut with the husk on and about 19.4 per cent of the hard nut minus the husk.

In another sample of fresh nuts the kernel was 12 per cent of the nut with the husk on and 30.4 per cent of the hard nut minus the husk. The kernel contained about 57 per cent fat. The fat content of the whole, therefore, was about 7 per cent and of the nut minus the husk about 17 per cent.

Less Nitrate of Soda to be Mined.

Advices from London is to the effect that, at a meeting of the nitrate of soda producers held in Iquique recently, it has been agreed to reduce the production by 10 per cent for the next six months. Those who have signified their willingness to come to this agreement represent 48,000,000 quintals per annum out of a total production of about 66,000,000. The producers claim that the Balkan war has had the effect of reducing the consumption of fertilizer generally, and the six months' restriction, as agreed upon, will only give the consumption time to recur to the normal level.

THE DETERMINATION OF SODIUM BORATE IN SOAP.*

By PAUL POETSCHKE.

The customary method employed for the determination of borax in soap has been to extract the dry soap with 95 per cent alcohol, or, the soap without drying is extracted with absolute alcohol. The residue, insoluble in alcohol, is then treated with water and the borate determined by titration. It has been assumed that borax is insoluble in alcohol, undoubtedly, from the fact that this statement appears quite generally in the text-books.

About a year ago the author had occasion to conduct quantitative analyses of quite a number of commercial borax soaps and it was soon established that extraction with alcohol was unsatisfactory, owing to the solubility of borax in this liquid, even if the soap was thoroughly dried and extracted with absolute alcohol. When chemically pure sodium borate was boiled with absolute alcohol and carefully filtered until the filtrate was absolutely clear, it was found that the filtrate upon evaporation left a residue which readily dissolved in cold water, gave an alkaline reaction to methyl orange and a positive test for boron. The same sodium borate which had been thus boiled with alcohol was treated twice in the same manner and the individual filtrates evaporated to dryness. Both of these filtrates gave a residue which was readily soluble in cold water, the latter solution giving an alkaline reaction to methyl orange and a positive test for boron. An alcoholic solution of boric acid left no residue on evaporation. This demonstrates conclusively that the material dissolved by the alcohol consisted of borax and that it could not have been due to free sodium by hydroxide or free boric acid.

Two samples of commercial borax soaps were thoroughly dried at 100° C. and extracted with absolute alcohol in a Soxhlet extractor. The insoluble residue and the alcoholic extract were separately analyzed for the quantity of borax contained in each. Table I gives the results of these experiments, together with the total borax content of the soaps as determined by the method described in this paper.

TABLE I.

Sample.	Borax in alcohol extract, per cent.	Borax in extracted residue, per cent.	Total borax in extract and residue, per cent.	Total borax content of soap, per cent.
A	0.40	1.47	1.87	1.87
B	2.53	8.18	10.71	10.88

It is seen from the data in Table I that the error resulting from the solubility of the borax in alcohol amounts to 21.4 per cent of the total borax content in A, and 23.2 per cent in B, and that the borax found in the residue and extract agrees well with the total borax content of the soap.

*Paper read before New York Section, American Chemical Society, May 9, 1913.

[5] "Determination of Boric Acid in Insoluble Silicates," E. T. Wherry and W. H. Chapin, J. Am. Chem. Soc., 30, 1687.

An attempt was made to determine the borax by ignition of the soap with alkali carbonates. The ash was dissolved in water, slightly acidified with hydrochloric acid and boiled under a reflux condenser in order to expel carbon dioxide. After neutralizing the excess of acid with sodium hydroxide, using methyl orange as an indicator, the boric acid was titrated with N/10 alkali in the presence of glycerine, using phenolphthalein as indicator. Owing to the presence of silica in the soaps, this method failed to yield satisfactory results.

Wherry[1] has described a volumetric method for the determination of boric acid in insoluble silicates and an adaptation of this method was found to yield satisfactory results. It was found that silica was not always present in the soaps in sufficient quantity to give a satisfactory precipitation, so that it became necessary to add a fixed quantity of silica to the alkali carbonate used in the fusion mixture. The method as finally developed is as follows:

Weigh 10 grams of the soap (or 5 grams if more than 5 per cent of borax is present) into a platinum dish and add 2.15 grams of fusion mixture (consisting of 200 grams sodium carbonate, 15 grams silica in fine powder). To this mixture add 15 cc. of alcohol, mix with the aid of a glass rod and after washing the rod with a little alcohol, evaporate the mass to dryness on the water bath. Ignite until the combustible material is destroyed, cover the dish with a piece of platinum foil and fuse. Completely disintegrate the fusion by boiling with water and transfer the solution to 250 cc. round-bottomed flask. Acidify with 20 cc. of dilute hydrochloric acid (1:1), heat nearly to boiling and add a moderate excess of dry precipitated calcium carbonate. Connect with a reflux condenser and boil vigorously for 10 minutes. Filter out the precipitate through a folded filter, washing several times with hot water, but keeping the total volume of liquid below 200 cc.

Return the filtrate to the flask; add a pinch of calcium carbonate and again boil under a reflux condenser. Remove the flame and connect the top of the condenser with a water pump. Apply the suction until the boiling has nearly ceased. Cool to ordinary temperature, add 50 cc. of neutral glycerine and titrate the solution with 0.1 normal sodium hydroxide, free from carbonate, using phenolphthalein as indicator. After the end point is reached add 10 cc. more of glycerine and again titrate. Repeat this process until the addition of glycerine causes no further action on the end point. The number of cubic centimeters required multiplied by 0.00955 will give the equivalent of borax ($Na_2B_4O_7.10H_2O$) present in the solution.

A number of analyses were made in which a definite amount of chemically pure borax was added to castile soap which was free from borax. The results of these determinations are given in Table II.

TABLE II.

Per cent sodium borate added.	Per cent sodium borate found	
	A	B
10	10.00	9.99
7	6.96	6.96
5	4.91	4.96
3	2.95	2.96
2	1.97	1.96
1	0.95	0.98

It is evident from the table that the method gives results which are in close agreement with the actual borax content of the soap.

It is always advisable to test a soap qualitatively for borax before undertaking the quantitative determination. This is accomplished by placing one gram of the soap in a test tube, together with 10 cubic centimeters of dilute hydrochloric acid. The mixture is then heated to boiling, which causes the fatty acids to rise to the surface. After cooling the tube under a tap of running water, the acid liquid is filtered through a wetted filter. A strip of turmeric paper is immersed in the filtered liquid and dried, when it will acquire a deep red color, which changes to green or blue on the addition of ammonia, if borax is present. A number of tests conducted with known amounts of broax show that the test performed in this manner is sensitive to 0.05 per cent of borax in the soap.

There is a considerable variation in the borax content of commercial borax soaps. Analyses of fourteen different brands are given in Table III.

TABLE III.

Laboratory number.		Per cent of borax.
79188	Borated skin soap	None
79189	Antiseptic toilet soap, borated	1.96
79190	Best borax soap	None
79191	Borax soap	0.17
79192	Finest quality borax soap	0.10
79193	Borax soap	1.85
79194	Real borax soap	10.88
79195	White borax soap	6.44
79196	Refined borax soap	1.35
79518	Best borax soap	0.03
79519	Best borax soap	None
79520	Borax soap	3.42
79521	Borax soap	None
79522	Borax soap powder	None
82569	Borax soap	None
82570	Cocoa borax soap	None
82571	Borax washing compound	None

It is thus apparent that a considerable number of the commercial borax soaps contain absolutely no borax, or practically none, whereas those which contain borax vary from 1.35 to 10.88 per cent.

In conclusion, I wish to acknowledge my indebtedness to my assistants, Messrs. J. A. Flanagan, M. J. Vinick and E. C. Pailler, for their assistance in the analytical work.

The Cross Fertilizer Co. of Nova Scotia in the first seven months of operation disposed of some 16,000 tons of slag fertilizer. In addition to the fertilizer plant the company has purchased an experimental farm to demonstrate the use and value of its products. The enlargement of the company's plant for the manufacture of mixed fertilizer, containing muriate of potash and sulphate of ammonia, together with other extensions, means an expenditure of $80,000.

A RAPID MODIFIED CHLORPLATINATE METHOD FOR THE ESTIMATION OF POTASSIUM.*

By W. B. HICKS.

HISTORICAL.

Many attempts have been made in recent years to develop a short practical modification of the chlorplatinate method for the estimation of potassium. These have proceeded along three essentially different lines, all of which have sought to avoid the necessity of estimating other constituents than potassium and sodium chlorides before undertaking the precipitation of the potasssium. The first two modifications, the shortened method of Fresenius and the Lindo-Gladding method, are so well known that they need not be discussed here.

In the third modification the potassium solution is evaporated directly with chlorplatinic acid, the residue washed with alcohol, the potassium chlorplatinate reduced and either the chlorine titrated or the platinum weighed. Although such a procedure has been the subject of numerous investigations in Europe, it seems never to have found its way into American literature. Because of this fact, and the rapidity, reliability and practicability of this procedure, the author feels justified at this time in directing attention to this excellent method, and in presenting the results of experiments along this line.

Finkener,[1] in 1866, first used a reduction method for the estimate of potassium. He evaporated the potassium solution with chlorplatinic acid, washed the residue first with alcohol and then with ammonium chloride solution, reduced the K_2PtCl_6 by igniting in hydrogen, extracted the residue with water and weighed the KCl, obtaining excellent results in the presence of various other salts.

In 1873 Mohr[2] proposed to precipitate, wash and dry potassium chlorplatinate in the usual way, then to mix this precipitate with sodium oxalite, ignite, leach out with water, acidify with acetic acid and titrate the chlorine, using K_2CrO_4 as indicator.

De Koninck[3] suggested, in 1881, to dissolve the potassium chlorplatinate in hot water, reduce with magnesium ribbon and titrate the chloride with silver nitrate solution. To avoid the formation of oxychlorides in the reduction with magnesium, Fabre[4] suggested the addition of a drop of sulfuric acid which should be neutralized by means of $CaCO_3$ previous to the titration with $AgNo_3$. Diamant[5] preferred to reduce the chlorplatinate solution with zinc dust rather than magnesium, because under the conditions no oxychlorides of zinc were formed. In a second investigation on the subject, De Koninck[6] effected the reduction of the chlorplatinate by warming the solution with calcium formate. Stolba[7] proposed, in 1884, to reduce the K_2PtCl_6 with amorphous silver. This reduction, according to Atterberg,[8] proceeds too far and is not to be recommended.

Many reduction methods in which platinum is weighed have been proposed. Thus Hilgarde[9] reduced the K_2PtCl_6 by heating, while Meissl[10] and Vogel and Haefcke[11] effected the reduction by heating the precipitate contained in a porous Gooch crucible in a current of hydrogen. Neubauer[12] substituted coal gas for hydrogen because it is more practical and gives equally good results. Sonstadt,[13] accomplished the reduction by heating the precipitate with mercury. In all cases after complete reduction the soluble salts were washed out and the platinum weighed.

In the wet way the oldest reduction method is that of Corenwinder and Contamine.[14] According to their procedure, the K_2PtCl_6 dissolved in hot water is added to a boiling solution of sodium formate. This method is often slow and leaves adherent deposits on the walls of the vessel which are difficult to remove according to Jean and Trillat,[15] who proposed to reduce the chlorplatinate by adding a few drops of formaldehyde to the solution made alkaline with soda. This effects immediate reduction, the authors contend, and the platinum comes down in large flocks which are easy to wash. Warren[16] used formic acid and ammonia to effect the reduction.

In 1867 Roussin and Comoille[17] suggested the use of magnesium as a means of reduction in analytical chemistry, and later Scheibler[18] used the metal in the analysis of gold and platinum salts of organic bases. In 1893 Villiers and Borg[19] adopted this means of reducing the chlorplatinate in the estimation of potassium, in which they added fragments of magnesium ribbon to the solution slightly acidified with hydrochloric acid until reduction was complete. The platinum was then filtered off and weighed. Atterberg[20] in a series of investigations on the best means of reducing the chlorplatinate in which a large number of reducing agents were tried out, concluded that magnesium, mercury and thioacetic acid are best suited for this purpose. Thioacetic acid gives a voluminous precipitate of platinum and is therefore best used only with small amounts of platinum. Mercury gives good results only when in considerable excess and in hot, concentrated solutions. Magnesium, on the other hand, gives equally good results under all conditions and is therefore preferable. Later, this method of estimating potassium has been the subject of investigations by Regel[21] Grete[22] and Fiechter.[23]

The question concerning what substances interfere

*From Journal of Industrial and Engineering Chemistry in which it is published by permission of the Director of the U. S. Geological Survey.

[1]Pogg. Ann., 9, 637, (1836).
[2]Z. anal. Chem., 12, 137 (1873)
[3]Rev. Univ. des Mines, 9, No. 2 (1881).
[4]Chem. Z., 20, 502 (1896).
[5]Ibid., 22, 99 (1898).
[6]Ibid., 19, 901 (1895).
[7]Ibid., 8, 456 (1884).
[8]Ibid., 22, 533 (1898).
[9]Hilgard, Versuchsstationen, 42, 174 (1893).
[10]Meissl, Ibid., 42, 173 (1893).
[11]Landw. Vers.-Sta., 47, 109 (1896).
[12]Z. anal Chem., 39, 481 (1900)
[13]J. Chem. Soc., 67, 984 (1895).
[14]Bull. de la Soc. Industrielle du Nord, 1879.
[15]Bull. de la Soc. Chim. de Paris [3], 7, 228 (1892).
[16]Chem. News, 75, 256.
[17]Z. anal. Chem., 6, 100 (1867).
[18]Deutsch. Chem. Gesell. Ber., 2, 295 (1869).
[19]Comp. rend., 116, 1524 (1893).
[20]Chem. Z., 22, 522 (1898); 22, 538 (1898).
[21]Ibid., 30, 681 (1906).
[22]Ibid., 34, 1040.
[23]Z. anal. Chem., 50, 629 (1911).
[24]Landw. Vers. Sta., 47, 109 (1896).

with the determination of potassium by the proposed method is an important one. Vogel and Haefcke[24] showed that sulphates do not interfere, while Neubauer[25] obtained good results in the presence of sodium, calcium and magnesium chlorides and sulphates and large quantities of sulphuric acid. Atterberg[26] determined potassium in the presence of iron and alumina after the addition of citric acid. Earlier Villiers and Borg,[27] working on known samples, obtained 100 per cent of potassium in the presence of sodium phosphate, sodium and aluminum sulphates, and sodium, calcium, magnesium and iron chlorides. The present investigation has confirmed the results of these authors and has slightly extended the list of non-interfering substances. As a matter of fact, the writer has found no salts which seriously affect the estimation of potassium by this method and it is possible that aside from rubidium, caesium, ammonium and organic compounds, no substances do interfere with this determination.

METHOD.

On the basis of the results in the literature cited above and of the outcome of experiments described below, the following procedure is recommended for the estimation of potassium. The method is applicable in the presence of chlorides, sulphates, phosphates, nitrates, carbonates, borates and silicates, salts of sodium, barium, calcium, strontium, magnesium, iron and aluminum, and is especially suited for the estimation of potassium in potassium salts, salines and mixed fertilizers in which only the quantity of potassium is desired, and also in organic fertilizers after an appropriate modification to remove ammonia and other organic bases which interfere with the determination.

The method follows: Prepare the solution in the usual way, acidify slightly with hydrochloric acid, add chlorplatinic acid solution slightly in excess of that necessary for the complete precipitation of the potassium present and evaporate the solution on the steam bath to a syrupy consistency, *i. e.*, until solidification occurs on cooling. Flood the cooled residue with a small quantity of alcohol of at least 80 per cent strength, grind thoroughly with a pestle made by enlarging the end of a glass rod, and allow to stand one-half hour. The alcoholic solution should be colored if an excess of chlorplatinic acid has been used. Pour the liquid through a small filter, using suction, and before adding more alcohol rub up the residue again with the pestle. Now continue the washing by decantation with small portions of alcohol until the wash liquid becomes colorless. Three or four washings usually suffice. Transfer the precipitate to the filter and wash two or three times with alcohol.

Dissolve the precipitate in hot water, washing it through the filter into a beaker of convenient size. To the hot solution add about 1 cc. of concentrated HCl and approximately 0.5 gram magnesium ribbon (which has been previously washed in water) for every 0.2 gram[28] potassium present, stirring the solution and holding the magnesium at the bottom of the beaker by means of a glass rod. When the magnesium has practically dissolved, add a few cubic centimeters of dilute hydrochloric acid and allow the flocculent platinum to settle. The supernatant liquid should be perfectly clear and limpid like water if reduction is complete. To make sure add more magnesium, in which case the solution will darken if reduction be incomplete. Now add concentrated hydrochloric acid and boil to dissolve any basic salts, filter, wash thoroughly with hot water, ignite and weigh. From the weight of platinum thus obtained calculate the per cent of potassium.

The writer carried out eight determinations in conjunction, filtering both the potassium chlorplatinate and platinum on paper, using a filter cone and suction pump, and finally igniting and weighing the platinum in porcelain crucibles.

EXPERIMENTAL PART.

To determine whether or not the common associates of potassium interfere with its estimation by the proposed method, three series of experiments were carrid out:

(1) Blank determinations on a number of salt solutions.

(2) Determination of potassium in known samples in the presence of various other substances.

(3) Estimation of potassium in natural brines and salines with and without the removal of other constituents.

For this purpose the following solution were prepared:

(1) Chlorplatinic acid solution containing one gram of platinum in 10 cc. of the solution.

(2) Potassium chloride solutions whose potassium content was carefully determined by repeated analysis.

(3) Solutions of the following salts: NaCl, Na_2SO_4, $CaCl_2$, $BaCl_2$, $SrCl_2$, $MgCl_2$, $AlCl_3$, $Al_2(SO_4)_3$, $FeCl_3$, Na_2HPO_4, $Na_2B_4O_7$, $NaNO_3$, and silicic acid.

Baker's analyzed chemicals were used for the preparation of these solutions with the exception of calcium, magnesium and aluminum salts, sodium sulphate and silicic acid, of which solutions were specially prepared to free them from potassium.

Blank determinations were made on each of these solution by evaporating a definite quantity with chlorplatinic acid and proceeding according to the method described above for the estimation of potassium. In all cases no residue of K_2PtCl_6 could be seen, but on washing the filter paper with hot water and reducing the filtrate with magnesium a few flocks of platinum were noticeable in some cases. The results of these blank determinations are given in Table I.

[25] Z. anal. Chem., 39, 481 (1900).
[26] Chem. Zeit. [2], 22, 538 (1898).
[27] Compt. rend., 116, 1524 (1893).
[28] Fletcher, Z. anal. Chem., 50, 632.

It will be observed that in no case is there more than a few tenths of a milligram of platinum. This trifling amount is to be attributed to small quantities of soluble chlorplatinates adhering to the filter paper or to traces of potassium in the salts themselves.

In the experiments on known samples the potassium chloride solutions used were first carefully analyzed with the results given below. The theoretical factors were employed in all cases in making the calculations.

TABLE I.

KCl solution Sol. No.	taken Cc.	K_2PtCl_6 found Gram	KCl calculated from K_2PtCl_6 found Gram	Platinum found Gram	KCl calculated from Platinum found Gram	Cl average Gram
1	10	0.6505	0.1995	0.2612	0.1995	0.1997
	10	0.6514	0.1998	0.2616	0.1999	
2	25	.....	.....	0.2626	0.2006	0.2005
	25	.....	.....	0.2623	0.2004	

TABLE I.

No.	Substance taken	Weight taken Gram	Platinum solution used Cc.	Weight of platinum obtained Gram
1	NaCl	0.2	1.0	None
2	Na_2SO_4	0.3	0.5	0.0003
3	$CaCl_2$	0.5	0.3	0.0002
		0.2	4.0	0.0002
4	$AlCl_3$	0.3	0.5	None
5	$Al_2(SO_4)_3$	0.3	0.5	None
6	$FeCl_3$	0.5	2.0	None
7	$Na_2B_4O_7$	0.3	0.5	None
8	$SrCl_2$	0.3	0.5	None
9	$BaCl_2$	0.3	0.5	0.0003
10	$MgCl_2$	0.3	0.5	None
11	Na_2HPO_4	0.4	0.5	0.0004
12	$NaNO_3$	0.5	0.5	0.0003
13	Silicic acid	5.0 cc.	0.5	0.0006
14	Boric acid + NaCl	0.2 + 0.3	1.0	None

TABLE II.

No.	Salts added	Quantity of salts added Gram	KCl taken Cc.	KCl taken Gram	Platinum found Gram	KCl calculated from Platinum found Gram	KCl recovery Per cent
1	NaCl	0.2	10	0.1997	0.2617	0.1999	100.1
		0.2	10	0.1997	0.2622	0.2003	100.3
2	Na_2SO_4	0.2	10	0.1997	0.2624	0.2004	100.4
		0.2	10	0.1997	0.2615	0.1998	100.1
3	$CaCl_2$	0.2	10	0.1997	0.2628	0.2007	100.5
		0.2	10	0.1997	0.2620	0.2001	100.2
4	$AlCl_3$	0.2	10	0.1997	0.2607	0.1992	99.8
		0.2	10	0.1997	0.2606	0.1991	99.7
		0.3	25	0.2005	0.2623	0.2004	100.0
		0.3	25	0.2005	0.2622	0.2003	99.9
5	$Al_2(SO_4)_3$	0.2	10	0.1997	0.2617	0.1999	100.1
		0.2	10	0.1997	0.2613	0.1996	100.0
6	$FeCl_3$	0.2	10	0.1997	0.2623	0.2004	100.4
		0.2	10	0.1997	0.2626	0.2006	100.5
7	$Na_2B_4O_7$	0.25	25	0.2005	0.2626	0.2006	100.0
		0.25	25	0.2005	0.2627	0.2007	100.1
8	$SrCl_2$	0.3	25	0.2005	0.2636	0.2014	100.4
		0.3	25	0.2005	0.2631	0.2010	100.2
9	$BaCl_2$	0.3	25	0.2005	0.2629	0.2008	100.2
		0.3	25	0.2005	0.2626	0.2006	100.0
10	$MgCl_2$	0.3	25	0.2005	0.2621	0.2002	99.9
		0.3	25	0.2005	0.2612	0.1995	99.5
11	Na_2HPO_4	0.1	25	0.2005	0.2611	0.1995	99.5
		0.4	25	0.2005	0.2631	0.2010	100.2
12	$NaNO_3$	0.3	25	0.2005	0.2637	0.2014	100.5
		0.3	25	0.2005	0.2612	0.1995	99.5
13	NaCl + Na_2SO_4	0.3 + 0.5	10	0.1997	0.2608	0.1992	99.8
14	Silicic acid	8.0 cc.	25	0.2005	0.2635	0.2011	100.3
		80 cc.	25	0.2005	0.2638	0.2011	100.3
15	Solution x (*a*).	0.5	25	0.2005	0.2618	0.2000	99.8
		0.5	25	0.2005	0.2621	0.2002	99.9

(*a*) Solution x represents a mixture of the following substances: H_2SO_4, NaCl, Na_2SO_4, $CaCl_2$, $MgCl_2$, $FeCl_3$, $AlCl_3$, $Na_2B_4O_7$ and Na_2HPO_4.

Definite quantities of potassium chloride solution and of other salts were mixed, evaporated with chlorplatinic acid, and the method prescribed above was followed. The results are given in Table II:

The figures indicate that the above-mentioned salts have practically no deleterious influence on the estimation of potassium, and that the method is sufficiently accurate for all commercial purposes.

In Table III are given the results of a few analyses obtained in checking up routine work.

TABLE III.

No.	Character of sample	Sample taken Grams	Total soluble salts present Gram	K_2PtCl_6 found Gram	Platinum found Gram	KCl calculated Gram	KCl Per cent
200	Earthy material	2.000	0.189	0.0805	.....	0.0247	1.24(*a*)
		2.000	0.189	.....	0.0318	0.0243	1.22
300	Earthy material	2.000	0.4320	0.1306	.....	0.0401	2.00(*a*)
		2.000	0.4320	.....	0.0505	0.0386	1.93
400	Earthy material	2.000	0.1303	0.1644	.....	0.0506	2.53(*a*)
		2.000	0.1303	.....	0.0670	0.0512	2.56
85	Brine	10.47	0.4782	.....	0.3139	0.2398	2.29
		10.47	0.4782	.....	0.3134	0.2394	2.29
		10.47	0.4782	.....	0.3123	0.2386	2.28
120	Brine	10.81	0.8765	.....	0.3593	0.2745	2.54
		2.70	0.2191	.....	0.0944	0.0721	2.67(*a*)

(*a*) All constituents except Na, K and Mg chlorides previously removed.

These experiments were carried out in connection with the "Potash Investigation" in the U. S. Geological Survey, so that the results illustrate the agreement that should be obtained in practice.

The method recommends itself from the fact that it is well adapted for the carrying out of a number of determinations simultaneously, it is accurate, it is rapid in that most associates of potassium do not interfere, and it requires a minimum quantity of chlorplatinic acid solution.

A public demonstration was given on July 11, 1913, of the workings of the sun-power plant recently erected by a New York concern at Meadi, near Cairo in Egypt. The principle involved in the plant is the invention of Frank Shuman, an American who supervised the erection of the plant and conducted the experiments. The plant covers several acres of land on the west bank of the Nile. A series of reflectors and absorbers, a low-pressure steam engine, a condenser, and a pump comprise the principal independent units of the mechanism. There are five reflectors, each of which is 204 ft. long and parabolic in form. They are spaced at intervals of 20 ft. and made up of a series of 1/8-in. glass mirrors. The reflectors aggregate a total light absorptive surface of 13,500 sq. ft., are placed in iron frames, and geared and interconnected with the engine by an arrangement of cog-wheels. The mirrors automatically follow the course of the sun and are regulated by what is termed a thermostat, the secret of the invention. Running exactly down the center of each reflector is the boiler or absorber, a box of 3/8-in. metal with a tube at the top. By means of an automatic feed the box is constantly half full of water.

METALLURGY.

DETERMINATION OF PHOSPHORUS IN STEELS CONTAINING VANADIUM.*

By J. R. CAIN and F. H. TUCKER.

*From Journal of Industrial and Engineering Chemistry.

It is known that vanadic acid, even when present in small quantity, interferes with the precipitation of phosphorus as phosphomolybdate. Where the quantity of phosphorus is small relatively to the vanadium, as in steel, the vanadium not only contaminates the precipitate which is obtained, but also retards the rate at which it is formed and may prevent complete precipitation.

While developing a method in this laboratory for the determination of vanadium by co-precipitation with phosphomolybdate,[1] it was observed that the vanadium is precipitated in this manner only when present in the quinquivalent condition; quadrivalent vanadium was not precipitated, neither was pervanadic acid. In some experiments made by adding enough hydrogen peroxide to a solution containing vanadium to convert all of it to the pervanadate, not the slightest co-precipitation was observed with large or small amounts of added phosphate. The precipitates of phosphomolybdate obtained had the normal canary-yellow color, in contrast to the orange-red tint of precipitates containing vanadium. Other tests also showed no vanadium in such precipitates.

These observations suggested the possibility of determining phosphorus in the presence of vanadium by converting the latter to pervanadic acid before adding the molybdate reagent. To test this question, determinations of phosphorus in the B. S. Vanadium Standard (No. 24), in the B. S. Chrome-Vanadium Standard (No. 30), and in some synthetic solutions containing varying proportions of iron, chromium and vanadium, were carried out by the alkalimetric method, except that the vanadium was converted, before precipitation of the phosphorus, to pervanadic acid by means of hydrogen peroxide. While this method yielded satisfactory results with the majority of the large number of samples tested, there were occasional irregularities which we were not able to eliminate. In cases where the method failed, the precipitates were red, the results were low, and no further precipitate formed after a long period of time. In a series of determinations with a given sample faulty results occurred only occasionally. A great deal of work was done in trying to find the causes of these apparently accidental failures by varying the concentration, temperature, acidity, etc., of the solutions, but without success.

Apparently the trouble is due to a decomposition of the hydrogen peroxide and of the peroxidized vanadium before complete precipitation of the phosphorus takes place, and this decomposition is probably caused by the presence of one or more of the numerous catalyzers which decompose hydrogen peroxide. Owing to this fact and to the further objection that hydrogen peroxide also peroxidizes the molybdenum of the precipitant, thereby causing possible abnormalities in the action of the latter, it was decided to abandon this method for general work. It is quite possible, however, that correct results on a given sample may be obtained by making several determinations and eliminating from the average those which are evidently wrong when judged by the criteria above indicated.

Experiments which resulted in the discovery of a satisfactory method based on reduction of the vanadium to the quadrivalent condition were then begun. The fact that phosphorus may be quantitatively precipitated by the molybdic reagent when present with vanadium in this condition[2] has long been known. We have found that the difficulty in applying this principle to the analysis of steel arises from the fact that whereas original solution of the metal must be made in nitric acid, if the direct molybdate precipitation is to succeed, the presence of this acid complicates the reduction of the vanadium as the operation is ordinarily carried out. It has often been attempted to reduce vanadium to the quadrivalent state by means of ferrous iron, but the statements in text-books referring to this method indicate, directly or indirectly, that success has not been attained. Thus, Johnson[3] states, and gives results indicating, that such reduction, as carried out in his experiments, did not give correct results for phosphorus. Brearley and Ibbottson[4] give determinations on two samples of ferrovanadium containing large amounts of phosphorus, where the vanadium had been reduced under conditions specified by them.

Whether or not the phosphorus content which Brearley and Ibbottson reported was correct cannot be deduced from their statements, for this element was not determined by any other method known to give a correct result. It is equally impossible to decide from their experiments whether the vanadium was completely reduced at the time of precipitation. If it was not completely reduced (causing low results for phosphorus), there would have been produced a corre-

[1] Cain and Hostetter, B. S. Tech. Paper No. 8; This Journal, 4, 250 (1912).

[2] Treadwell, "Kurz, Lehrbuch der Analy. Chem.," pp. 227 and 228, 4th ed., Vol. II, 1907.

[3] "Chemical Analysis of Special Steels, etc.," pp. 22 and 23, 1903.

[4] "The Analysis of Steel Works Materials," p. 166, 1902.

[5] Loc. cit., p. 165.

sponding amount of the orange-colored precipitate which always forms in the presence of vanadic acid, but this, when associated with the large amount of normal phosphomolybdate which they obtained (their samples contained 0.65 per cent and 1.35 per cent phosphorus, respectively), might easily have escaped their notice. From other statements made by Brearley and Ibbottson on this subject[6] it would appear that they believe the formation of an orange-colored precipitate has little significance in affecting phosphorus results, the deficiency in phosphorus precipitated in such cases being compensated by the positive error caused by the vanadium associated with the precipitate. In this connection it may be stated that our results show that formation of a red or orange-colored phosphomolybdate always indicates incomplete precipitation of the phosphorus.

Having confirmed, by a series of results, the fact that phosphorus is quantitatively precipitated as phosphomolybdate in the presence of quadrivalent vanadium alone, the disturbing factors operating when vanadic acid is reduced by ferrous iron in nitric acid solutions of steels as a preliminary to the determination of phosphorus were investigated.

Duplicate nitric acid solutions of steel containing added vanadic acid were reduced with excess of ferrous sulfate. To one of the pair there was added the usual proportion of ammonia used in a regular phosphorus determination, and, after cooling, the color of the solution was compared with the companion solution to which no ammonia had been added. Not only had the blue color of the first solution due to reduced vanadium disappeared, being replaced by the yellow tint of vanadic acid, but the treated solutions usually gave but a slight test for ferrous iron. It thus appears that quadrivalent vanadium is oxidized by the nitric acid when the solution is heated by adding the necessary amount of ammonia. The vanadic acid thus formed would have prevented complete precipitation of phosphorus; moreover, most of the excess of ferrous iron, which would have tended to keep the vanadium reduced, had disappeared.

Solutions of steel containing vanadium and phosphorus were then prepared for precipitation of the latter by reducing with ferrous sulfate under the proper conditions to insure an excess of the reducing agent being present at the time of adding the molybdic reagent. When precipitation was made at 35° to 45° C., the solutions usually gave no test for ferrous iron after completion of the five-minute period of shaking generally recommended. When the reducing agent had thus disappeared, the oxidation of the hypovanadic acid was indicated by change in color of the solution, by abnormal color of the precipitate, and by low results. However, if precipitation was made at 15° C., excess of ferrous iron was almost always present.

We sought to determine whether phosphorus may be quantitatively precipitated as phosphomolybdate at low temperatures. With prolonged and thorough shaking or agitation of the solution, quantitative precipitation can be made at temperatures of 15° to 20° C., and our successful determinations, given in Table I, have been made at these temperatures. A 10-minute shaking suffices; the precipitate thus formed settles rapidly and filters as readily as that formed at 35° to 45° C., as in the ordinary procedure for determining phosphorus in steels.

Even with an excess of ferrous iron, as indicated by the ferricyanide drop test, red or orange-colored precipitates and low results were often obtained. The solutions in such cases had a deep red color. There was a strong odor of oxides of nitrogen and sometimes even evolution of these gases. It was evident, then, that under certain conditions vanadic acid in nitric acid solution would not be completely reduced by ferrous iron, even with a considerable excess of the latter present. The trouble was found to be caused by the presence of oxides of nitrogen, due to interaction of ferrous iron and nitric acid; for when the gases were expelled from the solution, for instance by passing carbon dioxide in the cold for a sufficient time, the deep red color disappeared, the phosphorus precipitates were normal in color, and the results were quantitatively correct. To further test this point, a vanadate solution was reduced by sulfurous acid, the excess of reducer removed, and the vanadyl solution thus formed added to the nitric acid solution of a vanadium-free steel. Oxides of nitrogen, formed during the solution of zinc in nitric acid, were passed into the solution thus prepared. A gradual disappearance of the blue color, due to reduced vanadium, was observed, and the phosphomolybdate precipitate obtained from the solution of the steel was orange-colored, both results indicating that the oxides of nitrogen had caused oxidation of the vanadium. Some experiments were also made by precipitating phosphorus from steels containing vanadium, by reducing the latter with an excess of ferrous sulfate, the flask in which precipitation was made being filled with carbon dioxide; under these conditions there was complete precipitation and the phosphomolybdate had the normal color. It thus appears probable that the nitric oxide (NO) formed by action of the ferrous salt in nitric acid serves as a carrier of atmospheric oxygen to the vanadyl compound.

The method of preparing solutions of steels for phosphorus determination in the experiments described above was the usual one of dissolving in nitric acid of 1.135 specific gravity, oxidizing with excess of permanganate solution, and destroying the excess of oxidizer (with simultaneous partial or complete reduction of the chromic and vanadic acids in solution) by ferrous sulfate, sulfurous acid, or a sulfite. After the observations above noted had been made, it was finally found that, observing the precautions shown to be necessary by the preceding experiments, samples in which the preliminary reductions of excess of perman-

ganate, manganese dioxide, etc., were made with ferrous sulfate almost always gave trouble through incomplete precipitation, red or orange-colored precipitates, etc., whereas, on the other hand, samples in which this reduction was made by sulfurous acid or a sulfite nearly always gave good results. In the latter class of samples, also, after addition of ferrous sulfate to complete the reduction of the vanadium before adding the molybdate reagent, no odor of nitrous fumes was noticeable. Experiments were then made with the idea of reducing the vanadium by sulfurous acid alone, without the use of ferrous salt at all. This can be done; the essential conditions are to keep the temperature of the solution low and to allow time enough. Phosphomolybdate precipitated from such solutions has the normal color, and precipitation is quantitative. On account of the long time necessary, however, reduction by sulfurous acid alone is not to be recommended for routine work.

Our conclusion, then, is that the presence of small amounts of sulfurous acid in the solutions where that reagent was used as a reducing agent for destroying permanganate, etc., counteracted the effect of, or prevented the formation of, oxides of nitrogen upon adding ferrous salt. The formation of these oxides being thus avoided, their effect in preventing complete reduction of vanadic acid by ferrous salt was eliminated, and hence correct results could be obtained for phosphorus.

As a result of these investigations, then, the following four conditions should be observed in precipitating phosphomolybdate in nitric acid solutions of steels containing vanadium by the method of reduction of the vanadium to the quadrivalent state:

(1) The temperature of precipitation should be held at a point (1° to 20°) where the nitric acid does not oxidize the excess of ferrous salt or the reduced vanadium before complete precipitation of phosphorus takes place; (2) the partial neutralization with ammonia, frequently used when phosphorus is precipitated as phosphomolybdate, must be made before reduction of the vanadic acid, otherwise the heat of neutralization causes reoxidation of most of the ferrous iron and reduced vanadium by the nitric acid; (3) care must be taken to prevent the action of oxides of nitrogen, formed by interaction of ferrous salt and nitric acid, on the reduced vanadium; since these substances seem to catalyze the oxidation of the vanadyl salt and may in some cases completely prevent precipitation of the phosphorus, owing to the large amount of vanadic acid so produced; (4) efficient means for shaking or agitation of the solutions in which precipitation is to take place must be provided. A fifth condition, not likely, however, to give trouble with ordinary care, is the avoidance of too great an excess of ferrous salt. Under certain conditions, not fully investigated by us, a large excess of ferrous iron in the presence of vanadic and molybdic acids causes reduction of the latter, which, of course, is to be avoided for the present purpose. When all these conditions are observed there is no co-operation of vanadium in solutions containing as high as 1.5 per cent of this element. This point was verified by testing phosphomolybdate precipitates (from a steel containing 0.112 per cent phosphorus and 1.5 per cent vanadium) for vanadium by dissolving the precipitates in concentrated sulfuric acid, adding a drop or two of nitric acid and heating till fumes were given off strongly; on cooling, no yellow color developed, showing that no vanadium had been coprecipitated.[7]

B. S. steel standards.	Vanadium present, per cent, approximately.	Chromium present, per cent, approximately.	Phosphorus present, per cent (certificate value)	Phosphorus found with— V present	Phosphorus found with— V + Cr present	Differences (in percentages on steel) with— V present	Differences (in percentages on steel) with— V + Cr present
V steel	0.15(a)	...	0.035	0.037	....	+0.002	.....
No. 29...	0.15(a)	...	....	0.038	....	+0.003	.....
Cr V steel	0.21(a)	1.35(a)	0.043	....	0.046	....	+0.003
No. 30...	0.21(a)	1.35(a)	....	....	0.048	....	+0.005
B. O. H. 0.2 C Renewal 11a	0.2	0.5	0.0082	0.007	0.008	—0.001	—0.000
	0.4	1.0	.....	0.008	0.007	—0.000	—0.001
	0.6	2.0	.....	0.008	0.006	—0.000	—0.002
	0.8	3.0	.....	0.008	0.010	—0.000	+0.002
	1.0	4.0	.....	0.007	0.008	—0.001	—0.000
B. O. H. 0.8 C Renewal 14a	0.2	0.5	0.2460	0.024	0.023	—0.001	—0.002
	0.4	1.0	.....	0.025	0.022	+0.000	—0.003
	0.6	2.0	.....	0.024	0.024	—0.001	—0.001
	0.8	3.0	.....	0.023	0.024	—0.002	—0.001
	1.0	4.0	.....	0.023	0.022	—0.002	—0.003
B. O. H. 1.0 C Renewal 16a	0.2	0.5	0.045	0.044	0.046	—0.001	+0.001
	0.4	1.0	.....	0.046	0.047	+0.001	+0.002
	0.6	2.0	.....	0.044	0.047	—0.001	+0.002
	0.8	3.0	.....	0.046	0.050	+0.001	+0.005
	1.0	4.0	.....	0.049	0.044	+0.004	—0.001
A. O. H. 0.2 C Renewal 19a	0.2	0.5	0.084	0.087	0.085	+0.003	+0.001
	0.4	1.0	.....	0.084	0.083	0.000	—0.001
	0.6	2.0	.....	0.084	0.083	0.000	—0.001
	0.8	3.0	.....	0.086	0.084	+0.002	0.000
	1.0	4.0	.....	0.084	0.083	0.000	—0.001
B. O. H. 0.2 C Renewal 9a.	0.2	0.5	0.112	0.106	0.109	—0.006	—0.003
	0.4	1.0	.....	0.111	0.117	—0.001	+0.005
	0.6	2.0	.....	0.111	0.109	—0.001	—0.003
	0.8	3.0	.....	0.110	0.116	—0.002	+0.004
	1.0	4.0	.....	0.106	0.106	—0.006	—0.006

(a) Certificate values.

The method, which is described below, is adapted to any steel containing vanadium, no other element which ordinarily complicates the determination of phosphorus being present. If tungsten, titanium, arsenic, tin, etc., are present, their disturbing influence is eliminated by the usual methods for steels containing no vanadium. Nickel, copper, chromium, molybdenum, or aluminum, when present as alloying elements along with the vanadium, do not interfere. The details of the method are as follows: The solution of the steel, up to the point where precipitation of the phosphorus is to be made, is prepared as for an ordinary phosphorus determination by the alkali-metric method, *viz.*, solution of 1 to 2 grams in 100 cc. of nitric acid (specific gravity 1.135), oxidation with slight excess of permanganate solution while boiling, destruction of the excess of permanganate, etc., by a

[7] Cain and Hostetter, loc. cit.

slight excess of sulfur dioxide or a sulfite, cooling of the solution and addition of 40 cc. of ammonia (specific gravity 0.96). Any steel which does not give all its phosphorus to the solution by this method must be treated in an appropriate manner, so that the acidity, concentration of ammonium nitrate, and total volume obtained are always the same as by the method of solution directed. Slight deviations from these conditions are, however, probably without significance. Assuming solution of the steel and partial neutralization to have been made as directed, the solution is cooled to 15° to 20° C., 5 cc. of a saturated solution of ferrous sulfate and two or three drops of concentrated sulfurous acid are added. After addition of 40 cc. of molybdate regeant the solution is shaken in an efficient manner for 10 minutes. The precipitate, after settling (which is quite rapid), is then filtered off, washed in the usual manner, and titrated by the alkalimetric method.

The following table gives results by this method on synthetic solutions made with B. S. standard acid open-hearth, basic open-hearth, and Bessemer steels, of varying phosphorus and carbon content, to which vanadium was added as sodium vanadate and chromium as chromimum nitrate. The acid and alkali solutions used for titrations were standardized against B. S. standard steels No. 19*a* (A. O. H. 0.2) and No. 9*a* (Bes. 0.2 renewal). The individual determinations in each series are single determinations only; the good agreement in all cases with the certificate values for phosphorus of the individual steels shows the reliability and accuracy of the method.

The time required is practically that for determining phosphorus in an ordinary steel.

The Director of Agriculture in Jamaica states, with regard to the cultivation of the castor bean in that island, that three of the best local varieties of these beans were tested at the Hope experiment station during 1912 and the returns of the seed per acre were very disappointing, although the plants grew luxuriantly. The best returns were one-third of a metric ton of seed per acre, and the director does not regard this as sufficiently remunerative to justify Jamaican planters in taking it up in place of the ordinary staple crops.

A company has just been registered in Paris with a capital of $2,219,500, which may be increased to $3,860,000, to take over several European textilose concerns. The combination will include the English Textilose Manufacturing Co. (Ltd.), Manchester; the Manufacture Francaise de Textilose, Paris; the Manufacture Belge de Textilose, Brussels, and the firm of Fratelli Borghi, Milan. The style of the new undertaking is the Societe de Textiloses et Textiles. The German works engaged in the manufacture of textilose are being considerably enlarged.

THE APPROXIMATE MELTING POINTS OF SOME COMMERCIAL COPPER ALLOYS.*

By H. W. GILLETT and A. B. NORTON.

In the course of investigations of brass melting furnaces it was necessary to determine the approximate melting points of a few of the common brasses and bronzes. The binary systems of copper-tin and copper zinc alloys have been thoroughly worked out not only as to melting points, but as to the full phase rule relationships, showing the different phases present in the solid alloys at different temperatures, and also as to tensile strength. The United States Alloys Research Board, under Thurston, studied the mechanical properties of the ternary systems of copper-zinc-tin alloys in detail, but as pyrometers were not perfected at the time of that investigation the temperature measurements were confined to very crude ones on the pouring temperatures of the two binary, copper-tin and copper-zinc systems, made by pouring the molten alloy into water, measuring the rise in temperature of the water and figuring the pouring temperature from the assumed specific heat of the alloy. The method, though the only one available at the time, was so crude and subject to so many errors that the figures are of little or no value. Experiments on the copper-zinc-tin system from the phase rule point of view are in progress at Cornell University, but no melting-point determinations have yet been made.

Thus, while the melting points of the two binary systems are well known, those of the commercial casting alloys containing copper, zinc, tin and lead, or copper with two of the other components, have had little or no study.

LACK OF DATA ON THE MELTING POINTS OF TERNARY AND QUARTERNARY ALLOYS.

Very few figures on the melting points of ternary and quartenary alloys can be found in the literature on alloys.

Primrose[1] mentions pouring gun-metal consisting of 88 parts copper, 10 parts tin, and 2 parts zinc, at 950° C. (1,740° F.),[2] this temperature being far too cold and giving a very poor casting of very low tensile strength, hence evidently not far above the melting point.

This figure is probably not correct, as an alloy consisting of 90 parts copper to 10 of tin has a melting point of about 1,005° C. (1,840° F.), and 2 parts of zinc would probably not lower the melting point to such a degree.

*Paper presented at the Annual Meeting of the American Institute of Metals, Oct. 13-17, 1913, Chicago, Ill. Published by permission of the Director of the Bureau of Mines. This paper is also published by the Bureau of Mines as Technical Paper 60.

[1]Primrose, H. S., Metallography as an aid to the brass founder: Metal Ind., vol. 8, 1910, p. 466.

[2]Since the accuracy of temperature measurements at the melting points of brasses and bronzes does not warrant figuring down to a degree, in transforming measurements taken in Centigrade or in Fahrenheit to the other scale, the results are calculated in round numbers to the nearest five or ten degrees.

Primrose[3] in a later paper shows a cooling curve for gun-metal containing 88 per cent of copper, 10 of tin and 2 of zinc, with less than 0.2 per cent of lead (exact analysis not given), which shows the melting point (liquidus) at 1,010° C., or slightly above that for a corresponding zinc-free bronze, although some lowering of the melting point by the zinc might be expected.

Longmuir[4] also poured some alloys at a temperature at which the metal would just flow, and so cold that in all cases the castings were poor and the tensile strength very low. The results obtained by Longmuir were as follows:

POURING TEMPERATURES OF FOUR ALLOYS.

Alloys.	Degrees C.	Degrees F.
Gun metal	965	1,770
Yellow brass	850	1,560
Red brass	1,058	1,935
Muntz metal	943	1,730

These figures also are probably not accurate. The remark made on the earlier figure by Primrose for gun-metal applies here. The composition of the alloys was not given. If it be assumed that the names given have their normal significance the yellow brass would be about 65 parts copper and 35 parts zinc, an alloy which melts at about 915° C. (1,680° F.), and the Muntz metal would contain 60 parts copper and 40 parts zinc, an alloy which melts at about 890° C. (1,635° F.). Muntz metal has a lower melting point than yellow brass, not higher, as shown by these figures. Similarly, red brass of the common composition, which is about 85 parts copper, 5 tin, 5 zinc and 5 lead, has a lower melting point than gun-metal (taken as 88 parts of copper, 10 of tin and 2 of zinc).

Karr[5] used a radiation pyrometer in determining the melting points and pouring temperatures of some copper alloys. For an alloy of 68.8 parts copper, 0.2 of lead and 31 of zinc, he gives 1,640° F. (895° C.), which is considerably lower than the true melting point, evidently because of the well known deviation from black-body conditions of molten copper or its alloys. He gives 1,650° F. (900° C.) as the melting point of one alloy containing 84 per cent copper, 1,735° F. (945° C.) for that of another of the same copper content, and 1,850° F. (1010° C.) for another said to correspond to gun-metal, but containing no zinc.

Karr's figures are confessedly inaccurate because of the deviation from black-body conditions, and in only one case is the exact composition of the alloy given.

Since the literature on the subject was found to be so meagre, it was decided to obtain figures on the melting points of a few typical commercial alloys with sufficient accuracy for the purpose in hand.

[3]Primrose, H. S., and Primrose, J. S. G., Practical heat treatment of Admiralty gun-metal; Jour. Inst. Metals (British), vol. 9, 1913, p. 169.

[4]Longmuir, P., quoted by Law, E. F., Alloys and their industrial application, 1909, p. 10.

[5]Karr, C. P., The pouring and melting points of some high grade bronzes: Trans. Am. Brass Founders' Assn., vol. 5, 1911, p. 78.

METHODS USED IN THE TESTS.

The alloys were melted in a gas furnace. Instead of using the ordinary shape of crucible which exposes too large a surface to volatilization and oxidation, crucibles were made up from some bonded carborundum tubes which were in stock from a previous investigation.

The carborundum tubes which are described in detail by Gillett[6] were about 4.5 cm. inside diameter and had about 8 mm. walls. They were cut to about 15 cm. long and an artificial graphite plug was fitted at one end to form the bottom, luting it into place with alundum cement. Considering the cost of machining out a crucible from a graphite rod, as well as that of the graphite itself, these were much cheaper than artificial graphite crucibles, especially as they do not burn away anywhere near as fast as graphite. Their life was as long as that of the ordinary crucibles of fire clay and graphite mixtures.

The temperatures were measured by a platinum, platinum-rhodium thermocouple used with a single pivot galvanometer.

The couple was calibrated against one which in turn had been checked against one calibrated by the Bureau of Standards, the secondary standard being read on a potentiometer, and the scale found to be correct within the limits of error of reading. The calibration was also checked up by reading the melting points of copper, of common salt and of a bronze of 90 parts copper and 10 parts tin. The scale was correct within the error of reading at these points.

As these calibrations were made with the cold junction at 20° C., the couple was used without placing the cold junction in ice water, the cold junction being so protected from the furnace that a thermometer at that point showed within 3° of 20° C. during all the runs.

The thermocouple wires were insulated by Marquardt tubing of 1 mm. bore and 2 mm. in outside diameter, and the hot junction was slipped into a Marquardt tube 30 cm. long and 9 mm. outside diameter and 5 mm. inside diameter closed at one end. The open end of this tube was fastened into an open ended porcelain tube 35 cm. long, 10 mm. inside diameter, 14 mm. outside diameter by alundum cement. This arrangement served to protect the couple from zinc fumes or reducing gases.

The end of the protecting tube was in turn protected from the molten metal by an artificial graphite boot, 9 cm. long and with 3 mm. walls.

There is a considerable time lag in the pyrometer reading when a cold protecting tube and boot is plunged into molten metal, but after the tube is once hot the lag is small. As the melting points were not determined by noting when the metal solidified, but by plotting temperatures against time, the proper

[6]Gillett, H. W., Temperature Measurements in an experimental carborundum furnace: Jour. Phys. Chem., vol. 15, 1911, pp. 225, 227.

temperatures for the heat evolution on freezing or heat absorption on melting should be shown even if there was some lag.

About 600 grams of steel was used in making the tests; the metals were weighed out in the proper proportions to form the alloy desired, a slight excess of zinc, increasing with the increasing zinc content, being allowed to compensate for volatilization. Electrolytic copper, Bertha zinc and chemically pure lead and tin were used. The copper was melted first, and covered with granular carbon and a little salt. When the copper was melted, the tin, the lead, and lastly the zinc, was added, and the alloy well stirred with a graphite rod.

When the alloy was fully melted and mixed, the pyrometer was inserted and so clamped that the graphite boot did not touch the bottom or sides of the crucible. The gas flame was lowered and the temperature read every 15 seconds, stirring between each reading. When the alloy had frozen the gas was turned up and a heating curve taken. This was repeated several times. Zinc was continually volatilized from the melts containing zinc, but not in sufficient quantity to exert appreciable influence on the melting point, as duplicate runs agreed within 5° C. in all cases. After the runs were completed, the melt was poured in most cases into an ingot mold, sampled and analyzed. As the analyses agreed well with the composition aimed at on the samples analyzed, the melts not containing zinc were not analyzed. Duplicate analyses of the same sample agreed within 0.1 per cent.

All the melts were made up from virgin metals except the sample of manganese bronze, which was in the form of test-bar ends from a previous investigation.[7] It had tested 76,000 to 77,000 pounds per square inch tensile strength and 24 to 35 per cent elongation in the standard brick-form test-bar. The bronze had approximately the following composition: Copper, 56 per cent; zinc, 41 per cent; iron, 1.5 per cent; tin, 0.9 per cent; aluminum, 0.45 per cent; and manganese, 0.15 per cent.

As it was first cast into an ingot, then remelted and cast into test bars, and these again remelted for melting-point determination, the zinc content was probably nearer 40 than 41 per cent and the copper nearer 57 than 56 per cent when the melting points were taken. This sample was not analyzed.

The melting point given is the liquidus, or point where freezing begins on cooling and ends on heating. This is more strongly marked than the solidus, or point where freezing ends on cooling or begins on heating. Fig. 1 shows one set of curves and the characteristic break at the melting point (liquidus).

These curves are typical of all melting point determinations.

RESULTS OF TESTS.

The data obtained in the determination of the melting points of several alloys were as follows:[8]

As the results all checked within 5° C., an allowance of ± 10° C. or ± 20° F. is probably ample to cover all errors of reading and of calibration and use of the pyrometer.

RESULTS OF MELTING POINT DETERMINATIONS OF 10 ALLOYS.

Alloy.	Composition aimed at, per cent. Cu.	Zn.	Sn.	Pb.	Composition by analysis. Cu.	Zn.	Sn.	Pb.	Number of duplicate determinations.	Melting point (liquidus). C.	F.
Gun-metal	88	2	10	..	....	....	....	...	4	995	1,825
Leaded gun-metal	85½	2	9½	3	85.4	1.9	9.7	3.0	6	980	1,795
Red brass	85	5	5	5	....	....	(2 samples)		8	970	1,780
Low grade red brass	82	10	3	5	81.5	10.4	3.1	5.0	4	980	1,795
Leaded bronze	80	..	10	10	....	....	....	...	3	945	1,735
Bronze with zinc	85	5	10	..	84.6	5.0	10.4	...	4	980	1,795
Half yellow, half red	75	20	2	3	75.0	20.0	2.0	3.0	3	920	1,690
Cast yellow brass	67	31	..	2	66.9	30.8	....	2.3	4	895	1,645
Naval brass	61½	37	1½	..	61.7	36.9	1.4	...	5	855	1,570
Manganese bronze	....	..	..	..	....	....	....	...	6	870	1,600

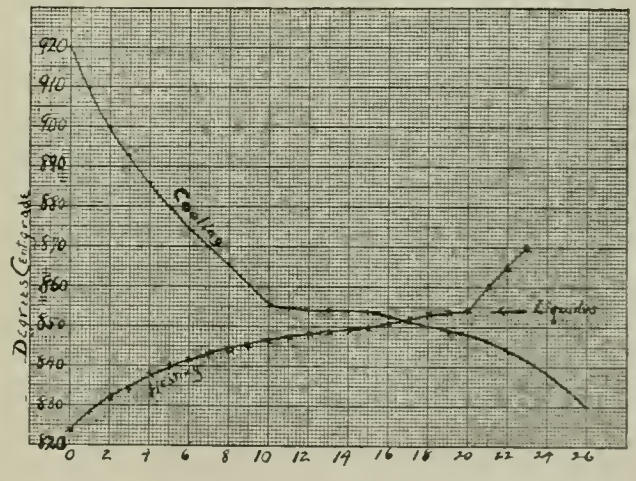


Fig. 1—Melting Point Curve for Naval Brass.

MELTING POINTS OF BINARY METALS FROM THE LITERATURE ON ALLOYS.

For comparison the melting point (liquidus) figures for binary systems of copper-tin,[9] copper-zinc,[10] and

[7]Gillett, H. W., The influence of pouring temperature on manganese bronze: Trans. Am. Inst. Metals, vol. 6, 1912, p. 207.

[8]The melting points and analyses in Table I were obtained by A. B. Norton, with aid from S. J. Popoff, at Cornell University, under the direction of Prof. W. D. Bancroft of Cornell University and H. W. Gillett of the Bureau of Mines, in the alloy work in which the Department of Chemistry at Cornell is co-operating with the bureau.

[9]Shepherd, E. S., and Upton, G. B., Tensile strength of copper-tin alloys: Jour. Phys. Chem., vol. 9, 1905, p. 446.

[10]Shepherd, E. S., The constitution of the copper-zinc alloys: Jour. Phys. Chem., vol. 8, 1904, p. 423.

copper-lead[11] alloys for the range covering the common industrial alloys are given below. These are scaled off from curves in the references given. As the curves are small, the figures are only accurate to within about ± 10° C. or ± 20° F.

MELTING POINTS OF 3 BINARY ALLOYS.

COPPER-TIN ALLOYS.

Parts by Weight.		Melting point.	
Copper.	Tin.	C.	F.
95	5	1,050	1,920
90	10	1,005	1,840
85	15	960	1,760
80	20	890	1,635

COPPER-ZINC ALLOY.

Copper.	Zinc.	C.	F.
95	5	1,070	1,960
90	10	1,055	1,930
85	15	1,025	1,880
80	20	1,000	1,830
75	25	980	1,795
70	30	940	1,725
65	35	915	1,660
60	40	890	1,635

COPPER-LEAD ALLOYS.

Copper.	Lead.	C.	F.
95	5	1,065	1,950
90	10	1,050	1,920
85	15	1,035	1,895

Although melting point determinations were made on only eleven alloys, those chosen represent a large proportion of the non-ferrous alloys in use in the ordinary foundry. Many of the other common alloys are near enough in composition to these or to the binary alloys, whose melting points are given, to allow obtaining the melting point by interpolation close enough for most technical purposes.

The United States Civil Service Commission, Washington, D. C., will hold an open competitive examination on Nov. 10 for assistant petroleum chemist, for men only. From the register of eligibles resulting from this examination certification will be made to fill a vacancy in this position in the Bureau of Mines, Department of the Interior, for service in the field (at San Francisco, Cal., or Pittsburgh, Pa.), at a salary ranging from $1,800 to $2,160 a year, and vacancies as they may occur in positions requiring similar qualifications, unless it is found to be in the interest of the service to fill any vacancy by reinstatement, transfer, or promotion. The duties of this position will be to assist in chemical researches in petroleum, and especially the refining of petroleum or petroleum products.

Infusorial or diatomaceous earth is made up largely of silica, is a variety of opal, and represents the remains of certain aquatic forms of plant life known as diatoms. Tripoli is a light, porous siliceous rock, supposed to have resulted from the leaching of calcareous material from the siliceous limestones, and is used as an abrasive, in the manufacture of filters, and in the paint industry as a wood filter, for enameling, etc.

[11]Desch, C. H., Metallography (Copper-lead alloys), 1910, p. 85.

WATER GAS TAR.*

The signal development of the water gas industry, since its advent to the present time, has evolved a significant factor in the manufacture of gas for illuminating and heating purposes. It has proven so successful that comparatively few gas works now rely entirely upon the destructive distillation of coal for their supply. In the United States alone over 300 plants are producing carbureted water gas only; and about 100 are producing both coal gas and water gas.

As long as the necessary oil is available, and obtainable at prices comparing favorably with gas coals, it seems we may look for maintenance of the present water gas plants, and for further installations, irrespective of new propositions for other methods by which to carbonize coal for obtaining coke and gas.

The extensive changes in the economics of gas manufacture have produced a comparatively new tar, which, during recent years, amounts to about 400 million gallons per annum, and the volume is still increasing. At first gas managers were confronted with a serious problem for the quick disposal of this tar, the only outlet seeming to be to burn it under boilers and such like places. Manufacturing chemists, who are ever on the alert for working up new or waste products, soon found that water gas tar was valuable for distillation, as it yielded, under careful and proper treatment, products almost (if not quite) identical with those obtained from ordinary coal tar, as produced in the retort system of coal gas manufacture; and at the present time many millions of gallons are annually worked up in this manner.

The tar distiller has thus materially helped in the progress of the water gas industry; in fact, so much so that the tar produced (almost valueless at first) at the present time commands a price per gallon not much less than that of coal gas tar, and it is now considered an important source of revenue to gas companies.

When water gas tar first became a commercial product it had to pass through the usual phases that attend any new product—prejudice, trial, adoption; and this took several years. After much controversy for and against it, water gas tar has been proven a commercial product of value, so much so that gas companies have little or no difficulty in disposing of all their production, mainly to tar distillers.

The process of manufacturing carbureted water gas, and the reactions involved, are well understood; particularly the chemical changes, which are recognized as the almost complete polymerization of the paraffines into members of the olefiant and benzene series of hydrocarbons. These being, to some extent, held by the hot gases in mechanical mixture, give the illuminating property to the gas produced in the generator. A considerable portion, however, is condensed in the cooling apparatus to liquid form, in the

*From American Gas Light Journal.

condition of a brownish-black, syrupy liquid, known commercially as water gas tar. This product, which contains also condensation and "drips" from the whole apparatus beyond the carbureters, is a product rather variable in physical character, particularly in specific gravity and water content. Such tars have been met with the specific gravity of which varied from 1.020 to 1.120. The water content frequently gives much trouble, both to the gas engineer and the distiller, as its complete separation from the tar is a difficult matter, owing to the strong tendency to form an emulsion, in which water may be present to the extent of 30 per cent to 40 per cent. In the larger gas works, where the most modern apparatus is installed and very large quantities of tar are produced, there is very little difficulty in obtaining a well dehydrated product.

Good water gas tar should not give over 0.5 per cent water on distillation, but distillers tolerate up to 2 per cent. This is a point which should be more carefully observed by gas engineers, because the question of water content is a serious one for tar distillers, and it certainly is a factor in the determination of value. As an average of laboratory tests of a large number of water gas tars received from various gas works, the yield in volume has been:

Constituent.	Per cent.
Water	1.25
Light oils	14.00
Dead oils	32.00
130° pitch	52.75
	100.00

This laboratory average very fairly represents the actual works distillation of about 5 million gallons in stills of 5,000 to 10,000 gallons working capacity.

The light oils, on re-distillation, yield about 60 per cent of crude naphtha, of a quality fit for the refinery. The dead oils, when first run, are clear, bright and quite light in color, and do not so readily deepen to the very dark brown shade as dead oil from coal tar does. The specific gravity of the bulk is rather lighter than the latter, ranging from 1.010 to 1.030, according to the quality of the tar and the method of distillation. Dead oil from water gas tar does not contain any "tar acids," but these can readily be added, to produce an oil with any desired percentage. This addition of acid to the neutral oil makes it equal to any coal tar oil containing tar acids, resulting from direct distillation. This is not supposition, but a fact confirmed by many years, production and use, that many of the coal tar creosotes, containing over 6 per cent to 8 per cent tar acids, have been fortified by the addition of these acids. The laboratory distillations of water gas tar creosote, to which tar acids have been added, show very clearly that it is practically identical with creosote from coal tar containing the same percentage of acids. This will be shown and discussed in another paper in the near future.

Pitch from water gas tar is splendidly clean. It contains only a very small percentage of carbon and has a bright, clean, fracture. It is tough and elastic, being more on the order of asphalt than is straight coal tar pitch, which, owing to the present day tars, is rather a scarce article. Water gas tar pitch, properly made and of the proper melting point, is just as valuable and perhaps more valuable for roofing, roads, and waterproofing purposes than the so-called "straight coal tar pitch."

Water gas tar has certainly had an uphill fight to prove its value; but, year by year, prejudice is decreasing, and extended trials made with it and its products have proven so satisfactory that now it can hold its own with coal tar. Water gas tar probably will never reach the price paid for coal tar, mainly because of the absence of the coal tar acids and the lesser yields of pitch. It has, however, become a staple commercial commodity, and gas managers need have no fear for the disposal of all they produce. They should, however, avoid becoming arbitrary, because, like other crude materials, there is a limit to its value, controlled by the market for the products obtained from it. They should also remember that it is the tar distiller who has, against long odds, created the demand and given this unexpected revenue to the gas companies that produce water gas.

PROGRESS OF GERMAN CHEMICAL TRADE.

The U. S. Consul General at Frankfort on Main, in a recent consular report, gives the following information on the German chemical trade:

The Frankfurter Zeitung recently reviewed at some length Germany's exports of chemical products with interesting figures showing the growth of this trade. The reviewer says, among other things:

The important inventions of Germany's chemists, especially in dyestuffs, and the country's monopoly of valuable potash salts make secure its position as first in the world's markets both for raw and for manufactured products in this industry. Even in those branches where patents have expired, as in the case of many dyestuffs, technical skill and perfection of factory processes have in the meantime secured for the German industry such an advantage that it is able to defy all competition, however vigorous it may be. Export figures show how rapidly the demand has increased for the products of the German chemical industry for which new markets are being constantly opened up.

IMPORTS AND EXPORTS.

The exports of chemical products from Germany during the first half of 1913 amounted in value to $114,994,000, as against $94,548,000 for the corresponding months of 1912 and $60,500,000 for the first semester of 1908. During the first half of the current calendar year products of the chemical industry formed 9 per cent of the Empire's total exports (as against 8 per cent six years ago) and showed a gain of 21.62 per cent over the corresponding half of 1912.

33.69 per cent over the first six months of 1911, and 9.95 per cent over January-June, 1908.

Imports also increased, but to a less degree than the exports. Thus for the first half of 1913 their value was $57,130,000, representing a gain of about 8 per cent over imports for the first six months of 1912 and an advance of 28 per cent and 54 per cent over the corresponding periods of 1911 and 1908, respectively.

Summarized, Germany's foreign trade in the more important groups of chemical products for the first six months of 1912 and 1913 was:

	Imports, first half.		Exports, first half.	
Groups.	1912	1913	1912	1913
Chemical raw products	$33,422,000	$39,149,000	$36,203,000	$46,919,000
Colors and dyestuffs	2,422,000	2,591,000	30,295,000	35,984,000
Varnish, lac, and putty	444,000	493,000	798,000	793,000
Ether, alcohols, etc.	6,232,000	6,649,000	3,607,000	5,071,000
Artificial fertilizers	3,187,000	3,781,000	6,402,000	6,143,000
Pharmaceutical products	4,530,000	4,267,000	9,674,000	11,963,000

THE MORE IMPORTANT ITEMS.

The items of chief importance in the export trade are chemical raw products and colors and dyestuffs, forming together about three-fourths of the total value. Exports of raw materials during the first half of 1913 showed a gain of about 30 per cent over the corresponding period in 1912, 32 per cent over the January-June portion of 1911, and 110 per cent over the first semester of 1908.

A marked increase was shown also in the various salts, such as chloride of potassium, etc. Belgium, France, and Austria-Hungary are the principal countries of destination of these shipments, while for salts to be used for fertilizers, which are also included in the export figures, the United States, Sweden, Russia, and Austria-Hungary are our chief customers.

CHEAP CITY GAS IN ENGLAND.

The Town Council of Widnes asks authorization of the British Local Government Board for making a loan to extend the municipal gas works, which are now worth $5,000,000. Enlargement of the present plant is necessary, owing to the great demand for gas, the annual sales of which have increased from 62 million cubic feet 31 years ago to 453 million cubic feet last year, and an estimated consumption of 520 million cubic feet this year.

The price of gas to the consumer in Widnes is said to be the lowest in the United Kingdom. While the rate in 1883 was $0.66 to $0.85 per 1,000, at present, it is $0.22 to consumers of 3 million cubic feet or more per annum, and $0.26 to ordinary consumers. The number of consumers in 1881 was 700, whereas last year the number was 7,830. Although the consumption of gas has increased by eight times, the gross capital has only increased two and one-half times—from $284,504 to $680,040. The capacity of the present plant is a little over 2 million cubic feet per day. The plant comprises 203 horizontal retorts, operated by manual labor. The capacity of the new plant will be 3 million cubic feet per day, and will be so constructed as to allow for an increased output of another million.

It is proposed that instead of merely adding to the present works, the whole of the old plant shall be superseded by a new equipment. The estimated saving to be effected by the new plant, based on results at other works, will be $40,000 per annum on the present output of gas. The engineer, in giving his reasons for preferring the system of horizontal retorts to the vertical, states that the only advantage to be gained by the adoption of the latter is a saving in ground space, and while this is most important in some places, such is not the case in Widnes, as the corporation has plenty of land. In addition to this reason, the engineer has recommended the adoption of the horizontal type in preference to vertical retorts or coke-oven plant, on the ground of economic working, efficient results, and low capital outlay. With the increased value of the residuals, owing to the new process, it is believed that the $0.09½, which represents the present cost price per 1,000 feet, will be still further reduced.

Construction of the new plant commenced in April this year, the contractors for the entire work being from Halifax, England, who expect to complete it in March, 1914. The carbonizing plant is divided into three sections, the first of which will be ready by the end of September, 1913. The whole of the old carbonizing plant will be thrown out of use and dismantled on completion of enough of the new plant to take the place of the old. The new plant is being erected on a separate site, adjoining the old works.

The engineer describes the type of the new plant now under construction as follows:

It is an improved system of horizontal retorts, with mechanical stoking and discharging machinery. The new retort house and coal store are being constructed adjacent to the gas works railway siding. End-trip wagons will discharge the coal into an underground hopper, which feeds the breakers, from which machine the coal will be elevated by a bucket elevator, and thence transferred by the push-type conveyors into overhead bunkers of an aggregate capacity of 500 tons, or two days' supply, the bunkers having controlled outlets which feed the traveling mechanical stoking and discharge plant of the Fiddes-Aldridge electrically-driven type. The retorts adopted are 20 feet through the sectional area, 24 by 20 inches, is in excess of the usual size. By the arrangement adopted, it is estimated that a charge of about 1 ton will be practicable, in a period of 12 hours, and that the carbonization will be almost continuous and steady, as in the case of the vertical retorts.

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NOTES AND COMMENTS.

Errata.

In the September number on page 90, in the article on "The Condensation of Gasoline from Natural Gas," by Burrell and Seibert, the temperatures stated in paragraph 2, second column, should be preceded by the minus sign.

Analyses of Coal in United States.

Government purchasing agents, designing and operating engineers, and the fuel departments of industrial concerns, large dealers in coal, and persons interested in the distribution and character of the different coals in the United States will find valuable information in a report just issued by the United States Bureau of Mines as Bulletin 22, entitled "Analyses of Coals in the United States, With Descriptions of Mine and Field Samples Collected Between July 1, 1904, and June 30, 1910." This report contains the analyses of 5,000 samples of coal taken from 1,500 coal mines and prospects situated in the various coal fields of the United States. Not only all of the important fields are represented, but practically all of the more important mining districts.

The purpose of the bureau of compiling and publishing this information is to present reliable information regarding the chemical composition and heating value of the coals. The samples of coals were collected by experienced men according to a definite and uniform system, and were analyzed under carefully controlled conditions, so that there might be no question as to the relative merits of the different coals so far as this can be determined by chemical analyses and determination of heating values.

The report just issued by the Bureau of Mines is in two parts, one giving the methods used in collecting and analyzing the samples, and the results of the analyses, and the other giving the exact location from which each sample of coal was taken, together with a description of the characteristic features of the coal bed at the point of sampling, the nominal capacity of the mine, and such notes on the preparation of the coal as might be useful to consumers.

Sulphur Production in the United States.

The production of sulphur in the United States in 1912 was 303,472 long tons, valued at $5,256,422, compared with 265,664 long tons, valued at $4,787,049, in 1911, according to W. C. Phalen, of the United States Geological Survey. The sulphur came from Louisiana, Nevada, and Wyoming, the production of Louisiana being the dominant factor in the domestic sulphur industry.

During the last 12 years the growth of the sulphur industry in the United States has been phenomenal, and the last 7 years has seen the dethronement of Sicily from the dominating position she so long held in the world's sulphur market. Within this period the United States has advanced from the position of an unimportant producer to that of one of the two leading sulphur producers of the world, owing entirely to the development of the sulphur deposits in Louisiana. In 1900 the sulphur production of the United States amounted to 3,147 tons; the imports during that year were 167,696 tons, of which 166,825 tons were classified as crude sulphur chiefly from Sicily. Thus the domestic production in 1900 amounted to not quite 2 per cent of the sulphur consumed. During 1912 the domestic production constituted more than 91 per cent of the consumption and the imports amounted to less than 9 per cent. Moreover, the imports of sulphur from Italy were only 8.7 per cent of the total importation, and Japan was the leading exporter of sulphur into the United States, 91 per cent of the foreign sulphur admitted having come from that country. It seems safe to predict that with the completion of the Panama Canal United States sulphur may practically displace foreign sulphur on the Pacific coast.

An advance chapter on Sulphur for 1912, just issued by the Geological Survey, includes detailed descriptions of the sulphur industry in Louisiana as carried on by the Union Sulphur Co. and an outline of the extensions of the company in Europe. An account of the beginning of the operations of the Freeport Sulphur Co. at Freeport, near Bryan Heights, Brazoria

County, Tex., is also included. This company began operations in November, 1912, when an initial run was made. The sulphur is to be obtained by a process similar to that employed in Louisiana—that is, it will be melted underground and pumped to the surface by means of an air lift. In Nevada the sulphur comes from the town of Sulphur, in Humboldt County. The Wyoming product comes from the Thermopolis district. A new deposit in Wyoming is located in Park County, 12 miles south of the deposits in Sunlight Basin.

Besides tables of domestic production the report gives figures showing the imports of foreign sulphur and the exports of domestic sulphur.

Mining in Sweden.

According to the annual report recently issued by the Bureau of Commerce and Industries (Kommerskollegium) of the Swedish Government, 300 iron mines were being worked during 1912. The total output of these mines was 6,699,226 metric tons of ore, of which 4,266,821 tons came from the mines in Norrbotten, the northernmost part of Sweden.

Thirty-four refining or enriching plants were in operation during the year, and 1,215,318 tons of raw ore was treated, resulting in the production of 520,710 tons of slig or refined ore, valued at $1,300,000. Compared with the production in 1911, this was an increase of about 39 per cent. The production of briquets of refined ore was carried on at 17 different works, the combined output for the year amounting to 288,553 tons.

The production of pig iron amounted to 699,816 tons, thus showing an increase during the year of 10.3 per cent. At Hoganas, 3,979 tons of iron sponge was produced.

During 1912, according to the report, the Swedish steel plants produced 63,900 tons of Bessemer ingots, 238,850 tons of Martin ingots and 4,850 tons of cast Martin steel. The total production of forged iron and steel amounted to 509,244 tons valued at $21,560,600.

With regard to the mining of other metals, results in 1912 were reported as, 2,877 tons of silver and lead ore, 3,059 tons of copper ore, and 50,000 tons of zinc ore. The coal mines in southern Sweden produced 360,291 tons of coal of different qualities, 135,773 tons of fire clay, and 58,846 tons of clinker clay. The value of the coal output was estimated at $750,400. Of the precious metals, 67,300 pounds of gold was obtained and 2,114 pounds of silver. The copper ore mined during 1912 yielded 4,352 tons.

Exportation of Malaysian Cultivated Rubber.

During the first seven months of the present year there was exported from the Federated Malay States 12,265 tons of cultivated rubber, against 8,071 tons during the similar period of 1912. The value of the exported rubber was $21,022,746, upon which the Federated Malay States have collected a duty of $524,567.

Process for Utilizing Waste Wood.

A writer in Paper gives the following information on a new process for utilizing waste wood:

A process has been worked in France on a semi-industrial scale for the manufacture of turpentine oil, resin products and cellulose from waste wood, *e. g.*, larch stumps yielding 30 per cent of ether-extract, the digestion being performed in a single operation. A description by Luttringer in the *Papierfabrik* is abstracted in the *Journal of the Society of Chemical Industry*. The digestion lye is composed of sodium hydroxide and sulphide, 60 to 100 kilos; carbonate, 30 kilos; sulphate, 50 to 200 kilos; water, 1,500 to 1,800 kilos. The pressure in the digester is gradually increased up to 5 to 7 atmospheres, the whole treatment occupying 6 to 12 hours.

During the digestion a slight escape of steam is permitted from the top of the digester through a cooling coil, so that the oil of turpentine distils over and is condensed. When the oil ceases to pass over, the valve is closed and the digestion of the wood is continued until complete. The spent lye, containing saponified and unsaponifiable resins, is concentrated and calcined, the volatile products of the destructive distillation being condensed while the residue is lixiviated for the recovery of sodium salts.

The condensed liquid consists of an aqueous layer from which methyl alcohol and acetone may be recovered. The tarry layer contains oils, phenols, etc.

Working with larch stumps on a scale of 500 kilos per charge, the following quantities of products were obtained per 1,000 kilos of wood: Cellulose, 315 kilos; oil of turpentine, 59.9; pine oil, 11.3; pinolin (rosin spirit), 13.8; light rosin oil, 8.7; ordinary rosin oil, 60; oil containing retene, 9.2; solid retene, 24; alcohol and acetone, 5.8; phenols, 15.7 kilos. The value of the oleoresin products exceeds that of the cellulose and products of a total value of about $31 are obtained from a ton of stumps.

New Modern Paper Mill in China.

A modern paper mill established by Chinese capitalists, including a number of Chinese in the United States, at Kongmun, a city on tide water in the Pearl River delta, has recently been put into operation. The plant has been in course of erection for some time under the direction of a Japanese company. The machinery which has been installed is German, though the Japanese concern erecting the plant has marked all machines with its mark. American machinery was sought at the time the contract was made for the plant and several bids were made, but American prices were rather too high, though the quality of American machines was considerably higher than that of the machines purchased. The mill has a capacity of about 15 tons of paper per week. It is using rags and rice straw for its pulp, and the quality of the output so far is considered very satisfactory. The supply of rags

is fair in quantity while the supply of rice straw is practically without limit, the only question being that of price for the products, and the price at present is satisfactory. The new mill has the advantage of water transportation for both its raw materials and its output. It is somewhat significant that the establishment is under the management of a Chinese engineer trained in Japan.

Wide Use of Arsenic

The United States produced more white arsenic in 1912 than ever before, the output for last year being 3,141 short tons, valued at $190,757, against 3,132 short tons, valued at $73,408, in 1911, according to a report on the subject by Frank L. Hess, just issued by the U. S. Geological Survey. The imports in 1912 were also the largest on record, amounting to more than 6,156 short tons, valued at $428,741, against 4,096 short tons, valued at $247,323, in 1911. The only white arsenic produced in the United States was that made as a by-product of smelting operations.

White arsenic is used principally in glass making and in the manufacture of Paris green, lead arsenate, and other insecticides. With the growth of horticulture and the necessarily greater attention paid to killing insect pests, the demand for arsenical insecticides has grown immensely. Experiments conducted by a number of the State agricultural experiment stations have demonstrated the value of arsenic when combined with lime as an effective spray against insect pests, while arsenic solutions have been found of considerable value when used as a dip for cattle and sheep.

A number of arsenic salts and oxides are used medicinally, among them the bromide, iodide, trisulphide, trioxide, sodium arsenate, and potassium arsenate. Disulphide or arsenic, both natural and artificial, is used as a paint pigment; in calico printing and dyeing; in tanning; and, as it burns with an intense white light, in fireworks. Orpiment, the trisulphide, called also king's yellow, is used as a paint pigment and as a reducing agent in chemical work. The trioxide is used in paints; for preserving hides, both for taxidermists and in the leather industry; as an antiseptic; and in killing animal pests. Sodium arsenate is used in dyeing with turkey-red oil and in printing fabrics; the arsenite in making soaps for use on skins and hides. Potassium arsenite is used as a reducer for silver in the manufacture of mirrors.

The Government's Classification of Coal.

The classification of coal into various grades, such as bituminous, semibituminous, and lignite, is arbitrary and unsatisfactory, but it is in common use in the United States, and in the absence of anything better it is published by the United States Geological Survey. The classes generally used in the United States are as follows: Anthracite, semianthracite, semi-bituminous, bituminous, subbituminous, lignite.

Anthracite coal is generally well known, but in a systematic classification it is generally defined as a hard coal having a fuel ratio (fixed carbon divided by volatile matter) of not less than 10. Most of this coal comes from the anthracite fields of eastern Pennsylvania, but small areas are known in some of the Western states where the coal has been changed to anthracite by the heat and pressure of masses of igneous rock.

Semianthracite coal has a fuel ratio ranging from 6 to 10. There is only a small amount of this coal in the United States, found in local basins or in close proximity to igneous rocks.

Semibituminous coal is of great commercial importance but is not widely distributed. Its fuel ratio ranges from 3 to 6. It is the best steam coal in the country, and some of it can be utilized in the manufacture of coke. The centers of production are the Pocahontas and new River fields of Virginia and West Virginia, the Georges Creek field of Maryland, the Clearfield of Pennsylvania, and the west end of the Arkansas field in the vicinity of Fort Smith. Though small areas containing coal of this grade have been found in Washington and Colorado, the amount of coal in these fields is small.

Bituminous coal is the most important grade of coal in the country and includes most of the coals east of the Rocky Mountains. In the Western States there are large areas of bituminous coal, such as the Trinidad-Raton field of Colorado and New Mexico; the Grand Hogback field of Colorado; the Book Cliffs field of Utah; Rock Springs, Kemmerer, and Black Hills fields of Wyoming; the Great Falls field of Montana; and many districts of Washington. This grade furnishes most of the coking coal of the country, and it is largely sold for steam raising and domestic use.

The term "subbituminous" has been adopted by the Geological Survey for what has generally been called "black lignite." The latter term is objectionable for the reason that the coal is not lignitic in the sense of being woody, and the use of the term seems to imply that the coal is little better than the brown, woody lignite of North Dakota, whereas many of the coals of this class closely approach the lowest grade of bituminous coal. In fact, it is extremely difficult to separate this class from the one below and the one above. It is generally distinguished from the lignite by its color and freedom from apparent woody texture and from bituminous coal by the slacking it undergoes when exposed to the weather. As the latter is an important difference in commercial use, it has been adopted by the Geological Survey as a criterion for the separation of subbituminous and bituminous coals.

Subbituminous coal is found in most of the western fields, being well known in the field about Boulder and Denver and in North Park, Colo.; Gallup, N. Mex.; Hanna, Douglas, Sheridan, and the Bighorn

Basin, Wyo.; Red Lodge and Musselshell, Mont.; and in many of the districts of Washington and Oregon.

As used by the Geological Survey lignite is restricted to the coals that are distinctly brown and generally woody. They are intermediate in quality between peat and subbituminous coal. Lignite is abundant in the North in eastern Montana and North Dakota and in the northwest corner of South Dakota. In the South it is present in all of the Gulf States, but it has been developed commercially only in Texas.

RECENT PATENTS.

The following patents relating to industrial and engineering chemistry are reported by C. L. Parker, 908 G Street, N. W., Washington, D. C.:

1,069,179. Process of *Roasting Ores* and Recovering Zinc Therefrom. C. J. Reed, Philadelphia, Pa. Patented August 5, 1913.

1,069,387. Steel *Process*. J. Churchward, Mt. Vernon, N. Y. Patented August 5, 1913.

1,069,498. Process of Treating *Ores*. C. C. Titus and W. J. Barenscheer, Helena, Mont. Patented August 5, 1913.

1,069,508. Manufacture of *India-Rubber* Goods. W. E. Windsor-Richards, London, England. Patented August 5, 1913. The process consists in heating in any suitable mixer a mixture of india-rubber and cellulose.

1,069,545. Method of Separating *Barytes* from Ores. C. J. Greenstreet, Webster Groves, Mo. Patented August 5, 1913.

1,069,809. *Storage Battery*. Wallace A. Prince, Quincy, Mass. Patented August 12, 1913.

1,069,951. *Caoutchouc* Substance and Process of Making Same. F. Hofmann and C. Coutelle, Elberfeld, Germany. Patented August 12, 1913. The process comprises heating erythrene under pressure until a caoutchouc-like substance results insoluble in acetone.

1,069,959. Process of Obtaining *Thorium*. M. Koss, Oranienburg, near Berlin, Germany. Patented August 12, 1913.

1,070,070. Production of *Nitrites*. Fritz Rothe, Dessau, Germany. Patented August 12, 1913.

1,070,258. Production of *Caoutchouc Substances*. F. Hofmann and C. Coutelle, Elberfeld, Germany. Patented August 12, 1913.

1,070,300. Production of *Aluminous Compounds*. H. Spence and W. B. Llewellyn, Manchester, England. Patented August 12, 1913.

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PROCEDURE OF THE U. S. ENGINEER OFFICE OF THE WAR DEPARTMENT AT ST LOUIS IN THE PURCHASE OF ILLINOIS COAL ON A HEAT UNIT BASIS.*

By J. M. GOLDMAN, M. E.†

The subject matter of this article deals entirely with Illinois bituminous coals purchased locally for steaming purposes by the U. S. Engineer Office of the War Department and powder producing corporations. The scope of the paper is limited to a resumé of geological conditions of the deposits, the heating value of the various coals, sampling in the mines and deliveries to consumers, the preparation of the samples, the laboratory scheme of testing, the fundamental characteristics of the coals with respect to purchase, and a method of comparing grades of coal by formula on the basis of heat units contained.

ILLINOIS COAL SEAMS.

The recognized number of coal seams in the Illinois field is 16, but those commercially available are only five namely; No. 1, No. 2, No. 5, No. 6, and No. 7. These seams are classified as follows:

Seam No. 1, underlying the counties of Rock Island, Mercer, Warren, McDonough, Fulton, Schuyler, Brown, Scott, Green, Calhoun, Henry, Jersey, Hancock and Christian. Tests from various mines in this seam show fair grade of coal containing 10-15 per cent moisture, 5 per cent sulphur, 8-10 per cent ash, and 11,000 B. T. U. per pound dry. This seam under normal conditions of mining is fairly clean and free from impurities.

Seam No. 2 underlies the counties of Bureau, LaSalle, Grundy, Will, Putnam, Stark, Marshall and Woodford. Analyses show good steaming coal containing about 15 per cent moisture, 2.8 per cent sulphur, 7.5 per cent ash, and 11,400 B. T. U. per pound dry. This seam is slightly better than No. 1, having less sulphur which occurs in coal in thin sheets of marcusite and pyrites, but the mine run product is apt to contain a higher ash content as the seam lies in two beds separated by shale partings ranging in thickness from 15 ins. to 20 ft.

Seam No. 5 is found in two districts, known as Central and Southern. The central district comprises Peoria, Fulton, Tazewell, Logan, Menard, Sangamon, and Macon counties, and the southern district comprises Saline and Gallatin counties. Tests of coal from these mines show content of 15 per cent moisture, 3.5 per cent sulphur, and 10.500 B.T.U. per pound dry. This is the poorest steaming coal in the field, as the seam is cut by numerous vertical clay veins, varying from a few inches to 4 ft. in thickness, and, in addition contains pyrites or "sulphur balls," and is capped by limestone, which if not cleaned from the coal after it is shot from place in the mine, causes pasty fusion of ash. and consequent clogging of air passages in grate bars.

Seam No. 6, west of the DuQuoin anticline, underlies the counties of Jefferson, Perry, Jackson, Franklin and Williamson, and east of the anticline in Sangamon, Christian, Mountrie, Shelby, Macoupin, Montgomery, Madison, Bond, St. Clair, Clinton, Marion, Washington, Perry, Randolph and Henry counties. The analyses of this seam show inconsistent heat values, ranging in places from good grades of steaming coal to very poor. An average number of samples tested show grade containing 10-11 per cent moisture, 3.5 to 5.5 per cent sulphur, 13.5 to 22 per cent ash, and from 9,000 to 10,500 B. T. U. per pound dry, for mine run product. This seam is commonly known as the "blue band seam" owing to a blue clay or shale parting 20 ins. above the floor of the mines. In addition the seam has limestone for cap rock, and there occurs in it sulphur balls occasionally 6 ins. in diameter. In places this seam is so persistent in slate bands and sulphur impurities that it can not be mined economically. This seam furnishes much of the coal to St. Louis and viciinty with some coal from the southern counties from the Big Muddy and Carterville districts.

No. 7 seam underlies Vermilion and Edgar counties principally, with Danville as a center. The tests on this seam show grade averaging 14 per cent moisture, 2-3 per cent sulphur, 9-10 per cent ash, and 11,200 B. T. U. per pound dry. The seam is thin, and the coal is poor and has no market outside of the counties of its production.

From the foregoing paragraphs it is seen that coal in the market may vary greatly in value as a fuel, and in order to determine intelligently the value for any

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†United States Inspector.

particular coal, sampling and testing are resorted to, to determine approximately the contents of the constituents, favorable or unfavorable to the proper and scientific controlled combustion of the coal in the furnaces under the steam boilers.

Inability to obtain representative samples of run of mine coal, at or in the mines, has been the cause of much friction over contract specifications, and the over-rating of the steaming value of coal by bidders to consumers.

Coal Operators' Method of Sampling.—The coal operators depend wholly on the reports of the different surveys for the assays of the face workings of the mines and these are taken in the following manner:

An oil cloth is spread on the mine floor immediately at the base of the seam, and a strip of coal 4 ins. to 6 ins. in width is picked down the entire length of face to a depth of 6 ins., having carefully on a first operation avoided weathered coal. In the process of cutting down from top to bottom, any bands of slate or shale, and sulphur balls, and other impurities which exceed in thickness ½ in. are thrown out. The total sample thus secured represents fairly and in a general way the average material which is accumulated from actual mining condition. But from the description of the seams, and the method of sampling, it will be evident that in reality the sample thus obtained must differ in certain particulars from the coal as mined and made ready for market. In this method of sampling there is lacking an agreement or rule governing the amount of "extraneous" matter, such as partings, slate or shale, "limey" roofs or dirt, all of which affect the grade of coal, and in consequence of the method and manner of mining, these impurities enter into and vary the samples of run of mine coal. Therefore, it is extremely pertinent to both buyers and sellers that the samples taken should accurately represent the values of run of mine coal under local mining conditions, and should not be picked samples from coal in any place in the mine.

Sampling Coal on Delivery.—Of equal importance with securing by the mine operator a representative sample of the coal to be sold, is the sampling of coal upon delivery. For the consumer many schemes of sampling by shovel, and use of mechanical samplers have been proposed for bulk deliveries on board cars, on steamboats and on barges. The following system is used locally by the U. S. Engineer office for sampling its coal upon receipt in bulk on barges, or on cars or on board steamboats. Separate samples are taken from each delivery and are forwarded in waterproof bags by parcel post to the U. S. Testing Laboratory maintained locally at the U. S. Engineer Depot for miscellaneous testing.

The samples must be taken before wetting down the coal and in the following manner: Pipes about 3 ins. in diameter by 6 ft. in length are driven in opposite sides of each carload or pile of coal on the cars, flatboats and barges, and the cores so obtained are collected in gross in a common dry receptacle. If the coal on the barges is not in piles, but spread on deck in a load less than 5 ft. thick, or carried in open barges, the samples must be taken at intervals not greater than 20 ft. on each side and not more than 5 ft. from the edge of the load. Coal in cars must be sampled by driving the pipes in three places not less than 10 ft. apart.

During the process of sampling, picking out of slate, sulphur balls, or other impurities or in any manner selecting special coal is strictly prohibited.

After collection, the gross sample is empetied out on an iron surface, clean, dry, and free from rust, and the coal is crushed to pass through a ¾-in. ring. After crushing, the coal is spread evenly over the iron, and by shoveling gradually from edge to center, formed into a conical pile, the top of which is leveled off and the material is again spread over one-half the space formerly occupied, divided by quartering to about 10-lb. lots, one of which is selected for testing.

It is the aim in all sampling and quartering to eliminate as much as possible the personal equation. Consequently, in arriving at a method of sampling in gross, pipe sampling seems nearest to the elimination of this factor over any other method yet devised, and although this method, it is acknowledged is not perfect, it seems that no other better has been offered by anyone.

In addition to the method of pipe sampling described, the U. S. Bureau of Mines has developed the "long" pile and "alternate shovel" method by which the coal is sampled at time of the unloading from railroad cars, ships, barges or wagons, during the process of unloading by a shovel or specially designed tool, which is used for taking portions or increments from 10 to 30 lbs. or from slack or screenings 5 to 10-lb. samples.

If desired the coal contractor may be present or represented to see that the increments are regularly, and systematically collected and that the entire delivery will be fairly indicated in the gross sample. The number and frequency of the shovel samples should be regulated so that a gross sample of not less than 1,000 lbs. will be collected. If the coal contains an unusual amount of impurities, slate, etc., and if the coal is very large it may be necessary to collect larger gross samples to 1,500 lbs. or more. For slack, screenings, etc., where impurities are fairly homogeneously mixed throughout the mass, a 600-lb. gross sample is recommended.

Samples smaller than 250 lbs. are mixed on an 8-ft. x 8-ft. canvas, by raising first one end and then the other, thereby rolling the sample back and forth. Some criticism has been made of the Bureau of Mines' methods owing to low market prices of coal, as the sampling methods are taken from treatises on ore sampling in which the crushed ore to be mixed and quartered is usually worth many times more than the coal. In producing this 1,500-lb. gross sample required,

it undergoes ten operations of mixing, crushing and quartering before reaching the laboratory. The time thus consumed is about 2 days' labor at $1.80 per day, and the cost of sampling alone is about 6.5 cts. per ton. Many private laboratories in this section of the country test coal for 1¾ cts. to 2½ cts. per ton, based on large unit deliveries.

Laboratory Testing Methods.—In all testing it is of utmost importance that the small portion taken for analysis shall accurately represent the average composition of the shipment. This is especially true for coal in which the sulphur and ash are irregularly distributed. Also, the amount of moisture in the coal and in the sample vary from day to day, depending on quantity of water, and the humidity of the air in the mine, exposure to sunshine or rain in transit, etc., and for this reason a sample of coal may have a different composition on arrival at destination from that possessed when mined. But the results of all tests from any samples of the same coal should agree if the sampling has been done always under the same conditions, and the results calculated to a dry basis. The coal samples on arrival at the testing laboratory are usually previously crushed to particles about 6 mesh or size of a pea, the entire sample weighing about 10 lbs.

After exposure to the air in the laboratory for an hour at about 70° F., the sample is crushed to 40 mesh, well mixed, and quartered. One quarter is reserved, ground to 100 mesh, and put in tightly stoppered bottles, from which gram portions are taken for the laboratory tests.

For determination of amount of moisture, 1 gram of the general sample is weighed in a platinum crucible, dried by heating for 1 hour to and at 212° F. The crucible is then cooled in a dessicator and weighed. The difference in weight is the moisture contained. Although seemingly a simple operation, the determination of moisture, if not carried through with great care and precision will, in calculating coal from wet to dry basis, alter the result about 100 B.T.U. for each 1 per cent of error. No special moisture sample is taken in this proximate method of analysis and the moisture in the finely ground sample is determined solely in order to calculate coal from wet to dry basis. From the great number of samples which have been taken in the Illinois mines, it can be safely said that these coals average 10 per cent to 15 per cent of moisture at the mine where the shipments originate, and lose 5 per cent to 10 per cent en route to destination. Moreover, the Government buys all coal f.o.b. place of consumption, and therefore pays no freight on the water contained in the coal.

In speaking of "wet" coal and "dry" coal, it is evident that these terms are generally not clearly understood. These terms have a specific meaning in engineering parlance. "Wet" coal defines the actual condition of coal as received and sampled before test. "Dry" coal is a calculated result obtained by subtracting from 100 per cent the amount of moisture from the calorimeter sample and dividing the remainder into the British Thermal Units contained in the coal "as received." The "dry" coal basis therefore establishes the base grade of the fuel, standardizes, and eliminates all variables due to moisture.

In the determination of amount of volatile matter, the residue after the moisture test, or, if preferred, a new test sample from which the moisture has been expelled, is placed in a 20-gram platinum crucible having a well fitted cover to prevent escape of solid particles, and heated over the full flame of a laboratory standard Bunsen burner for seven minutes. The loss in weight is the content of volatile matter. The bottom of the crucible should be 25 cm. above the top of the burner and the flame should be about 10-15 cm. long, and the determination made in a room free from draughts.

Such determinations of volatile matter, however, are open to criticism as there are possibilities of oxidation of the contents, with too great a heat, incomplete combustion, or other variances caused by quality of flame, and shape of crucible. The probable limit of variation in tests above is 1 to 5 per cent.

Sulphur determinations are made from bomb residues of Parr calorimeters in a specially designed sulphur photometer. The specific amount of sulphur in coal is needed in computation of the British Thermal Units as will be explained in the paragraph on the heat calculation. The sulphur is also accounted for, partly, in the volatile matter, and in the ash, and a determination is made especially for the total content contained in the coal.

The fixed carbon represents the difference obtained by subtracting the determined percentage of moisture, volatile matter, and ash from 100 per cent. The fixed carbon in coal is variable depending on the moisture and volatile matter. After the above constituents of the coal have been combusted there remains the ash, the negative index of the value of the coal.

In the ash determination, the coal is placed in a platinum crucible and is burned to black slag in the presence of oxygen supplied from a low pressure tube. This method reduces the sample to ash in about five minutes, minimizing errors and standardizing the results. Other methods of burning the sample from three to four hours over a Bunsen burner result 1½ to 2 per cent more ash than when using oxygen. In justice to coal operators, the oxygen ash determination, as approaching more closely the furnace reduction of the fuel, should be made standard and specified in all coal contracts.

Determination of the British Thermal Units to be derived from a pound of coal is made by use of an instrument called a calorimeter, of which there are many types in use. The Bureau of Mines use the oxygen bomb type, also many municipal laboratories, as a greater range of precision has been attained with this type of machine than with any other. The Parr calorimeter has given satisfaction, as its commercial

range of accuracy on the same sample is well within reasonable limits, and it can be installed and operated more economically than the oxygen bomb type.

In manipulating the Parr calorimeter, the directions furnished with the instrument are followed exactly, and, briefly, are as follows: A 0.5 gram sample, moisture free, is mixed with one 30 gram measure of sodium peroxide, and one gram of an accelerator, and the whole charged in the steel bomb. The bomb is placed in a can containing exactly two litres of water and revolved until the water has reached a constant temperature. The charge is then fired by electric fuse, and the bomb revolved in the can for three minutes, after which the thermometer readings are taken and the maximum rise in temperature is noted. The temperature results so obtained are used in a formula by which the British Thermal Units per pound of coal are calculated as follows:

1. Reaction in bomb after firing =
   73 per cent of heat due to *combustion of coal.*
   27 per cent of heat due to reaction of CO_2 and H_2O in contact with Na_2O_2.
2. Weight of water in can = 2,000 grams
   Weight of bomb complete = 135 grams
   (equivalent to specific heat heat of metal)
   System sensitive to heat....2,135 grams
3. $\frac{0.73 \times 2{,}135}{0.5 \text{ (grams sample)}} \times r\ (F^\circ) = \text{B.T.U.}$
   per pound of coal.
   r = corrected rise (F°)

v = initial reading
p = maximum rise from a constant temperature sustained three minutes after firing—usually 3° to 4° F.
v — p = r.

4. From r (F°), the following correction increments subtracted are made for highly volatile bituminous coals:
   Each 1 per cent ash multiply by.....0.005° F.
   Each 1 per cent sulphur multiply by...0.010° F.
   Each 1 gram accelerator ($KClO_3$)....0.234° F.
   Electric fuse .....0.014° F.
   Hydration factor (water in chemical combination) .....0.045° F.

In preparing coal specifications the moisture, volatile matter, ash, sulphur and fixed carbon must be carefully considered, but as in all government contracts, coal is purchased on a dry basis, as has hereinbefore been stated, and the limits for moisture have not been prescribed.

CHARACTERISTIC OF ILLINOIS COALS.

By close inspection of a hundred or more analyses of Illinois coals, the following characteristics of the constituents enumerated are evident:

1. Illinois coals are uniformly high in volatile matter and low in fixed carbon.

2. The volatile matter and fixed carbon vary inversely, and coal high in volatile matter runs low in heat units, and therefore a high fixed carbon content is index to heating value.

3. Coal with high ash runs high in sulphur, also the ash and sulphur contents vary directly with each other and inversely with the heat value (B. T. U.'s).

In view of these facts and of the necessary qualities of good steaming coal, the U. S. Engineer Office specifications are limited to a consideration of the ash, and the British Thermal Units of the coal. In this manner, the amount of heat the coal will furnish per pound, and the residue after combustion are obtained, the fixed carbon, volatile matter and sulphur being accounted for in the gross British Thermal Units derived in the bomb calorimeter, as in the fire box itself.

In view of inverse ratio between the ash and British Thermal Units, seconded by a knowledge of the mines from which the coal is mined, there is in this vicinity a strong tendency among local consumers to purchase coal on an ash basis alone. The practicability of this suggestion is doubtful where large quantities of run of mine coal are required, and it may be suggested that this method of test is better adapted to the purchase of screenings.

STANDARD GRADES AND SPECIFICATIONS FOR ILLINOIS COALS.

A careful study has been made of the Illinois coals and the resulting tests have guided in establishing the following standard grades and specifications for such coal:

1. Screened lump. The coal shall have been passed over screen openings 2 ins. square, and shall not contain more than 10 per cent slack, 12½ per cent ash, nor less than 11,500 B.T.U. per pound dry.

2. Run of mine. The coal to be the entire unscreened product as mined under normal conditions, and not to contain more than 40 per cent slack, 15 per cent ash, nor less than 11,000 B.T.U. dry.

3. Screenings. The coal shall have passed over screen openings ¼ in. square, and not contain more than 60 per cent slack, 22½ per cent ash, nor less than 10,000 B.T.U. dry.

Slack, in these grades, is defined in the specifications as all coal that will pass readily through screen openings ¼ in. square. The amount of slack in each delivery can be estimated with a fair degree of accuracy, but if necessary to be determined near the points of division (10 per cent, 40 per cent, 60 per cent), actual screenings of a sufficient quantity of coal to determine the grade should be resorted to.

A delivery of coal offered in one grade containing more slack than is allowable for that grade may be accepted for use, but will be paid for in the lower grade to which it has been determined that it belongs; and the contractor, provided he has no contract for such lower grade, will be paid therefor on the basis of a price in the same proportions as to his contract

for the same grade offered, as are the contract prices for the same grades of coal at the nearest point where such contracts are in force.

In the standard limits specified in the previous paragraphs relating to maxima for ash and minima for British Thermal Units, should the number of British Thermal Units in any delivery, as determined by analysis fall below the limiting number guaranteed therefor by the contractor, deductions for such deficiencies will be made from the price bid and stated, as follows:

Deficiency, B. T. U'S per lb. less than guaranteed minimum.	Deductions in percentage of price bid for each 100 B. T. U. to nearest 100 B. T. U. deficiency.
50- 549	1
550-1,049	1¼
1,050-1,549	1½
1,550-2,049	1¾
2,050-2,549	2

Should the percentage of ash in any delivery, as determined by analysis, exceed the limiting maximum guaranteed therefor, further deductions of 5 per cent of the price bid will be made for each 1 per cent of excess ash.

Standard specifications have been issued recently (by the Bureau of Mines) in which the canvassing of bids for award of contracts and fixing of penalties is adjusted to a comparative basis of 1,000,000 B.T.U. and the ash to an arbitrary scale. The criticism, in part, is that in canvassing the bid for heat value, the adjusted value of the coal corrected for moisture is multiplied by 1,000,000 and divided by the product of 2,240 multiplied by the number of British Thermal Units guaranteed. This method, however, does not convey any fixed idea of unit cost factor to a business man, nor bear any other relation to fuel calculation, and an expression of British Thermal Units to be received for each cent (or dollar) in payment would be more easily comprehended than a price stated for 1,000,000 B.T.U. In adjusting the grades with reference to ash the comparison is based on the highest percentage of ash in coal acceptable under specifications. In this manner the most inferior coal offered is taken as the standard for comparison, and on any fluctuating price from one bid to another prevents a comparison of prices. In payments, the ash is given an arbitrary fixed value of 2 cts. a ton penalty for each one per cent above or below the grade guaranteed by bidder. This scheme is probably best suited to coals of the eastern fields, in which the ash is uniformly low and its variation small. Owing to the "limey" nature of the Illinois coals, the tendency of the ash to fuse and clinker and the consequent choking of air passages through grate bars, the percentage of ash reflects highly the fuel utility of the coal, and affects the efficiency of the boiler. A differential of 2 cts. a ton is therefore a pure arbitrary without direct relation to the value of the fuel.

The heating value of the Illinois coals under consideration has been examined graphically in relation to their ash content, and the resultant curves show that the value of coal with 35 per cent to 40 per cent ash content, although still containing 2,000 to 3,000 B.T.U. is worthless for steaming purposes. Steaming tests conducted by the Bureau of Mines have confirmed this graph. Therefore, 40 per cent ultimate analysis of ash has been accepted as that per cent at which the value of coal as fuel disappears. As the average ash content of these coals is about 15 per cent to 20 per cent, it is evident that the rate of loss in value is fairly represented by a reduction of 5 per cent in price for each 1 per cent excess of ash above these average contents.

Comparing Grades of Coal by Formulas on Heat Unit Basis.—In comparing bids, all the variables—ash, calorific value, and price per ton—should be merged into one figure, the cost of the actual British Thermal Units for 1 ct. Accordingly, the following formula has been devised in which the inverse ratio between the ash and the calorific value has been maintained and reflected in the cost of heating value for a standard commercial unit:

$$\frac{TU}{p - \frac{(A - G)\,p + b + rm}{E}} = V, \text{ in which}$$

T = pounds per ton = 2,000.
U = British Thermal Units per pound, limiting minimum guaranteed by bidder.
p = price per ton expressed in cents.
A = maximum allowable percentage of ash.
G = percentage of ash, limiting maximum guaranteed by bidder.
E = percentage of ash at which value of coal as fuel disappears = 40 per cent.

Fixed charges:

b = rate per ton for barge service = 20 cts.
r = rate per ton-mile for barge towage — ¼c downstream = ½c upstream.
m = miles of barge towage to point of delivery.
V = comparative heating value offered by bidder for 1 ct. at point of use.

To illustrate the formula and show its significances the following bids are compared for run of mine coal:

Company.	Price per ton.	Guaranteed ash, maximum.	Guaranteed B. T. U.'s, minimum.	Method of delivery.
A	$2.00	13%	11,500	Cars
B	1.70	15%	11,000	Cars
C	1.60	15%	11,500	Cars

Case A:

$$\frac{11{,}500 \times 2{,}000}{200 - \frac{15 - 13}{40} 200} = \frac{23{,}000{,}000}{190} = 121{,}000 \text{ B. T. U.'s for 1 ct.}$$

Case B, by above formula, 129,400 B. T. U.'s for 1 ct.
Case C, by above formula, 143,800 B. T. U.'s for 1 ct.

On the basis of the standards set, coal "A," compared in price with coal "C," has same number of British Thermal Units with difference of 2 per cent in ash, and for each 1 per cent ash difference, the coal by inspection is actually worth $1.90 a ton. Coal "B" is similar in ash with coal "C," but has 500 less British

Thermal Units, consequently on basis of value of 1 per cent for each 100 B.T.U. the value of coal is lowered by 5 per cent of $1.70 or 8½ cts. to $1.615 per ton. Thus the contractors overrated coal "A" 10 cts. a ton and coal "B" 8½ cts. a ton. It is evident that coal "C" containing 143,800 B.T.U. for 1 ct. was awarded the contract.

OUR RADIUM RESOURCES,*

By CHARLES L. PARSONS.†

The "wonders of radium," both fact and fable, have been treated so extensively in the scientific and public press that it is not my intention, nor is it at all necessary, to repeat them here. Rather it is my wish today to present to a body of men interested in the development of American mining the present commercial situation as regards radium and its ores, and to point out, so far as I may, some of those future developments that already begin to be more or less distinctly visible.

A bulletin on the radium, uranium and vanadium situation, by R. B. Moore, physical chemist in charge of the Denver office of the Bureau of Mines, and K. L. Kithil, mineral technologist of the bureau, will appear within a few weeks and will contain much detail of interest to the mining industry. Last April an advance statement, authorized by the director, regarding this bulletin, brought out particularly the fact that practically all of the carnotite ore mined in the world in 1912 was shipped abroad and that this country was furnishing annually nearly three times as much radium from its Colorado carnotite deposits as all the rest of the world put together. It was further pointed out that this material has been bought by European buyers at a price entirely incommensurate with its radium value and that efforts should be made to keep at home both the radium itself and the profits of its manufacture; also that too much stress could not be laid upon the extensive waste of valuable radium ore thrown on the dumps of mines and prospects—much of it under such conditions that it could never be recovered.

The publication of this statement has already resulted in an increase of at least 33 per cent in the price of carnotite ore, and European buyers are awakening to the fact that they must pay to the American miner a price nearer the actual value of his ore. Also, a much lower grade of ore is now marketable, for whereas six months ago ore containing 2 per cent uranium oxide was the lowest grade accepted by European buyers, agents of these buyers are now asking for and actually purchasing ore containing no more than half this content of uranium. Furthermore, the operators are taking more care in separating their low grade ore from the gangue and in protecting it from wind and weather. Moreover, old dumps are being sold and ore that a few months ago was thrown aside as valueless will be recovered from them.

In this paper I shall refer to other facts contained in this bulletin and shall mention some new developments having a direct bearing upon the American radium industry which have taken place since the manuscript was sent to the printer.

As is well known to all of you, the popular belief has been that the chief source of radium is the mineral pitchblende, especially that obtained from the mines now under the control of the Austrian government of Joachimenthal, Bohemia, and pitchblende is the richest and most eagerly sought uranium radium ore. Outside of the ore in Austria, the only pitchblende deposits of any size are those in Gilpin County, Colorado, from which some thirty tons, more or less, have been procured since the mineral became valuable as a source of radium. The Denver papers recently announced that these pitchblende bearing mines have been acquired by Alfred I. du Pont, of Wilmington, Del., and it is greatly to be hoped that their exploitation under his direction will yield an increased supply of this valuable mineral. It is not, however, so generally recognized that the mineral carnotite, which, outside of the United States, occurs only in the Olray district of South Australia and in low grade ores mixed with ilmenite as a calcium carnotite (communicated by W. F. Hillebrand) under the name of Tyuyamyunite, in Ferghana, Russian Turkestan, low-grade ore mixed with ilmenite, is by far the more important source of radium. From the most authentic sources it can be definitely stated that the Australian and Russian deposits do not compare in extent or richness with our own. The American carnotite is accordingly the largest source of radium at the present time, and at least four times as much radium was mined in America in the form of carnotite in 1912 as has been produced from Colorado pitchblende since it was first discovered in that state.

Outside of carnotite and pitchblende, the only other known source of radium is the mineral autunite. The autunite deposits of Portugal have probably furnished a few milligrams to commerce, and from the Mt. Painter deposits in South Australia a few tons of autunite-bearing ores have been shipped to London.

American carnotite is found chiefly in Montrose and San Miguel counties, Colorado, and in Utah, northwest of these counties. The Utah deposits are at Green River, Table Mountain, Richardsons, Fruita, Moab, and some sixteen miles southeast of Thompsons. The ores of these deposits are of a lower grade than those of the Paradox Valley, but they are nearer to the railroads and transportation costs are much less. The Green River deposits have apparently become regular producers. In Colorado, prospects have been opened at Coal Creek, fourteen miles north of Meeker, and at Skull Creek, sixty-five miles west of

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†Chief of the Division of Mineral Technology, U. S. Bureau of Mines.

Meeker, but the richest of all American carnotite localities and, indeed, the richest known radium-bearing region in the world, is that of the Paradox Valley, extending from Hydraulic on the north to the McIntyre district on the south.

Geologists are now in the field making a special study of these carnotite ores with special reference to their occurrence and origin, of which altogether too little is now known. In the Paradox region, the deposits seem to lie invariably just above the fine-grained LaPlata sandstone. This rock is usually exposed high on the sides of the canyons, some of which are excelled in extent and in natural beauty by only the Grand Canyon itself. In a few instances, as at Long Park and Club Ranch, the deposits are only a few feet under the surface, the higher formations having been eroded; but for the main part, the stratum in which the carnotite occurs, when not entirely eroded, is deep below the surface of the mess. Accordingly prospecting is mainly carried on along the sides of the canyons, and where vanadium and uranium stains are seen upon the rock the prospector blasts his tunnel in the hope of developing a pocket of the ore. The fact that the ore occurs in pockets renders prospecting uncertain, and there appears to be no present hope of insuring a successful search for pockets that are not exposed, or do not happen to be near the surface. Although it is probable that many other pockets of carnotite occur at the same geologic horizon, their discovery, except where the ore-bearing stratum has been exposed by erosion, appears at present to be an almost hopeless task. The eroded sides of the canyons have been prospected again and again, but now claims are still being opened and are being sold by the prospector to the larger companies or operators who mine the ore. In such a sale the prospector and the purchaser both take a decided risk, for at present no method is used to determine the extent of the ore in the pocket other than the "prospector's hole."

As few of the prospectors of the west are acquainted with carnotite and pitchblende, the following description of the ores has been issued from the Denver office of the Bureau of Mines and is sent to all who make inquiry:

"In reply to your letter for information concerning radium ores, the following facts may be of interest:

"Radium is found with uranium minerals only. Wherever uranium exists, radium is also found in the mineral; and where there is no uranium, radium has never been found. Uranium and therefore radium are found in this country in carnotite and its associated minerals, and in pitchblende. Carnotite is a lemon-yellow mineral, usually found in pockets of sandstone deposits. The mineral may be in the form of light yellow specks disseminated through the sandstone, or as yellow incrustations in the cracks of the sandstone; or may be more or less massive, associated with blue, black, or brown vanadium ores.

"Pitchblende is a hard, blue-black ore that looks something like magnetite, but is heavier. It is found in pockets and veins in igneous rocks. This mineral is not nearly as widely distributed as carnotite. Occasionally it is found associated with an orange mineral called gummite.

"The best way to test these ores is to wrap, in the dark, a photographic plate in two thicknesses of black paper. On the paper lay a key and then, just above the key, suspend two or three ounces of the ore, and place the whole in a light-tight box. Pressure of the ore on the key and plate should be avoided. After three or four days, develop the plate in the ordinary way; and if the ore is appreciably radio-active, an image of the key will be found on the plate.

"The U. S. Bureau of Mines, 502 Foster Building, Denver, Colorado, will be glad to receive any samples of ores giving promise of containing radium and associated rare minerals, as indicated by the test above described. Though it cannot undertake to make chemical analyses or assays of such minerals for private parties, it will indicate the advisability of further examination."

The Colorado carnotite deposits were apparently first noted as far back as 1881, when Andrew J. Talbert mined some of the ore and sent it to Leadville, where it was reported as carrying $5 in gold per ton. This must have been an unusual ore, as the carnotite now found does not carry the precious metal. In 1896, Gordon Kimball and Thomas Logan sent specimens to the Smithsonian Institution, Washington, D. C., and were informed that the minerals contained uranium. Shortly thereafter they mined 10 tons of ore, shipped it to Denver, and sold it for $2,700 on account of its uranium content. Three years later, in 1899, Poulot and Voilleque collected and sent to France specimens which were examined by Friedel and Cumonge, who recognized the existence of a new mineral and named it "Carnotite" in honor of M. Carnot, then president of the French Republic. In 1900 Poulet and Voilleque leased carnotite ores at Cashin in the Paradox Valley to extract the uranium. They shortly after completed a small mill in the McIntyre district, south of the Paradox, and in this project had the co-operation of Jas. McBride, a mining engineer of Burton, Mich. Their mill ran until 1902 and during that time produced 15,000 pounds of urarium oxide. The mill was started again in 1903 by the Western Refining Company, but ran only a year. Up to 1904 the mills appear to have been run wholly with the idea of obtaining the uranium and vanadium from the ore, for no radium was extracted. Shortly afterwards the Dolores Refining Company built a new mill a short distance from the old one, but after running for some years, this mill, too, shut down. In 1912 the American Rare Metals Company acquired the mill of the Dolores Refining Company and is now operating it, with the special purpose of obtaining radium from the ores. The first attempt to

extract radium in this country appears to have been made by the Rare Metals Reduction Company, under the management of Stephen T. Lockwood, of Buffalo, N. Y. In September, 1900, Mr. Lockwood brought back from Richardson, Utah, samples of carnotite ore and in 1902 he published in the *Engineering and Mining Journal* of September 27th the first radiographic plate from products of American carnotite. In June, 1902, he received 500 pounds of specially picked high-grade ore from Richardson, Utah, and in May, 1903, as a result of experimental work on this ore, he incorporated what was probably the first American company to operate a plant to produce radium as one of its products. In October, 1903, the first experimental plant was constructed and in April, 1904, the first 17-ton car of ore reached Buffalo from Richardson, Utah. The company obtained a fair percentage of extraction, but the ore proved to be too low grade and the Richardson deposits were abandoned. No radium in concentrated form was put upon the market, although barium sulphate concentrates were produced.

The General Vanadium Company, which, with the Radium Extraction Company, is a subsidiary of the International Vanadium Company of Liverpool, England, was formed in 1909 and began work in 1910, the same year that the Standard Chemical Company of Pittsburgh, Pa., entered the field. Since that time these two companies have been engaged in mining carnotite. The ores from the General Vanadium Company have been shipped almost entirely abroad, while the Standard Chemical Company has shipped several hundreds of tons of carnotite to its works at Canonsburg, Pa. While it was stated at the time of the advance announcement of the bulletin to be issued by the Bureau of Mines, that one American Company had actively entered into production of radium, no actual sale of American produced radium could be authenticated. Since that time, however, the Standard Chemical Company has entered the American markets

Besides the American Rare Metals Company and the Standard Chemical Company, a third company—the Radium Company of America, with mines near Green River, Utah—has undertaken the production of radium in its plant at Sellersville, Pa. There is, therefore, every reason to hope that more and more of our ores will be worked up at home.

Besides the companies already mentioned, a number of independent operators mine and ship carnotite from the Paradox region and for the main part send their ores to Hamburg. Among the more prominent of these may be mentioned:

T. V. Curran, Placerville, Colo.
W. L. Cummings, Placerville, Colo.
O. B. Wilsmarth, Montrose, Colo.
David Taylor, Salt Lake City, Utah.

The costs of mining, and especially of transportation, are an important factor in the marketing of carnotite. The Green River deposits have a distinct advantage over the Colorado deposits in this respect, as they are nearer the railroad, but, as their ores do not average so high in uranium, this advantage is more apparent than real. The present costs of mining, sorting and sacking in the Paradox apparently vary from about $28 to $40 per ton. To this must be added an $18 to $20 hauling charge to Placerville, and, in most instances, an additional charge for burros from the mines to points that can be reached by wagon. The freight rate from Placerville to Hamburg, via Galveston, is $14.50 per ton, so that the average cost at present to the miner laying down his ore at the European markets approximates $70 per ton. The selling price varies with the uranium content, but is by no means proportional thereto, since a premium is always paid for rich ores. Very recently, however, a decided improvement has taken place and for 2 per cent ore, the price is now around $2.50 per pound for the contained uranium oxide, with an allowance of about 13 cents per pound for the vanadium oxide content, so that the 2 per cent ore will now bring in Hamburg about $95 per ton. One per cent ore is now salable, but unless this ore is taken from the dump, so that the mining cost may be disregarded, it will scarcely bear present transportation charges from the Paradox, although it is more than probable that it will be soon shipped regularly from the Utah field.

A price of $95 at Hamburg for 2 per cent ore leaves a fair margin of profit to the miner, as mining profits go, but when it is considered that this price represents only a little over one-sixth of the value of the radium content of the ore, that from this fraction of the value the American miner has to meet the outlay represented by the investment, by mining costs, transportation and assay costs and by losses in transit, it seems scarcely just that nearly nine-tenths of the value should go to foreign manufacturers of radium, especially when the fact is considered that radium can be produced much more readily from carnotite than from pitchblende. There are two ways of reducing this difference between the actual value of the ore and the price that the miner receives. One is to hold our American ores for a higher price, and the second is to manufacture radium at home.

Large wastes are still taking place in the mining of carnotite, owing to the inability of the low-grade ores to bear transportation charges. As has already been pointed out, however, a distinct improvement in this respect has taken place within the last few months. The miners are beginning to realize the value of their old dumps and are attempting to save the low-grade, non-shipping ore in such ways as will render its marketing possible when prices advance. The Bureau of Mines has done everything it can to impress the necessity of this truest kind of conservation upon the mine operator.

In addition, there is prospect that most of the low-

grade ores can be successfully concentrated by mechanical methods and experiments at the Denver office of the Bureau of Mines indicate that a concentration of four to one can be obtained. In this concentration, however, there are losses which could be prevented by chemical concentration, but at the present time it costs more to ship the necessary chemicals to the mines than it does to ship the ores to places where these chemicals can be cheaply obtained. It would appear, however, that mechanical concentration can save at least one-half of the material that is now going to waste.

Although, until recently, the manufacture of radium from carnotite has been carried on almost wholly in France and Germany, there appears to be no good reason why our American carnotite should not be treated at home. Carnotite is much more easily treated than pitchblende and the essential features of methods for its chemical treatment are well known, although much of the mechanical detail of operation has been kept secret. As the mechanical requirements, however, are those which any well-grounded chemical engineer should be able to solve, there seems to be no good reason why any of our carnotite ores should be shipped abroad, even at two or three times the present market price of the material. As before stated, the essential features of chemical methods of extracting radium from its ores are well known. As regards the principles involved, the methods have advanced little beyond the original method published by Debierne.

The methods for carnotite may be described best in the words of Soddy, in an extract from "The Chemistry of the Radio Elements," by Frederick Soddy, page 55, published in 1911 by Longmans, Green & Co.

"The most important operations in the working up of radium-containing materials are the solution of the materials, consisting usually of insoluble sulphates, and the separation of the halogen salts of the alkaline-earth group in a pure state, followed by their fractional crystallization. The first operation is usually effected by vigorous boiling with sodium carbonate solution filtering and washing free carbon sulphate. This is the well-known reaction studied dynamically by Guldberg and Waage, whereby an equilibrium is attained between the two pairs of soluble and insoluble sulphates and carbonates. Naturally the greater the excess of sodium carbonate the larger the proportion of insoluble sulphate converted into insoluble carbonate. In this operation it is advisable not to wash at once with water, but with sodium carbonate solution until most of the sulphates are removed, as thereby the reconversion of the carbonates back into insoluble sulphates is largely prevented. In dealing with crude materials—for example, the radium-containing residues from pitchblende—it is often advantageous to precede this operation by a similar one, using a sodium hydrate solution containing a little carbonate, which dissolves part of the lead and silica present. The carbonates, washed free from sulphates, are treated with pure hydrochloric acid, which dissolves the alkaline-earths, including radium. From the solution the latter may be precipitated as sulphates by sulphuric acid and reconverted back into carbonates as before, or sometimes more conveniently they may be precipitated directly as chlorides by saturating the solution with hydrogen chloride. This is a very elegant method of great utility in the laboratory, for the most probable impurities, chlorides of lead, iron, calcium, etc., remain in solution and only the barium and radium chloride are precipitated, practically in the pure state, ready for fractionation."

The price of radium appears for some time to have been holding steady at about $120 per milligram of radium metal. This does not mean that the material is bought in the elementary condition, but that the radium chloride and radium bromide, which are on the market, are paid for on the basis of the metallic radium they contain. This method of payment is a distinct advance over the old method of paying the same price indiscriminately for the chloride or bromide. This price of $120 per gram of the metal is equivalent to approximately $91,000 per gram of radium chloride ($RaCl_2$), or $70,000 per gram of anhydrous radium bromide ($RaBr_2$). Whether this price will rise, fall, or remain stationary can not be predicted. There is no question that there is to be an increased radium production and that meso-thorium is also coming upon the markets in increasing quantity, but the uses of and demand for radium are apparently developing at an even greater rate. Furthermore, the supply of the material is limited and no large resources are in sight. Only one estimate has been published of the total quantity of radium in the Colorado carnotite deposits and that was 900 grams. This estimate is at least five times as large as has been made by any employee of the Bureau of Mines, reckoning all known deposits in the whole American field, even including material too low grade to be marketable. Besides the radium, the uranium and the vanadium present in carnotite are available assets, and recent developments indicate that all the uranium produced will soon be readily sold, while it is well known that there is a ready market for vanadium for vanadium steel.

The value to the public of these deposits is, however, not to be measured in dollars and cents. The value of the radium output of America will never compare with that of several of our common metals. The total value of the radium in the world's output of radium ores in 1912 was little more than $1,000,000. Accordingly the value must ever be reckoned in what it can accomplish for the public knowledge and the public weal. No certain prediction can be made of the ultimate value of radium, or of its possible applications to science or medicine, but enough has been done to show that radium is worthy of the

fullest investigation by our higher scientific and medical authorities. Developments in its application to medicine are coming fast. The foreign medical press contains many apparently authentic reports of cures by its use. Interesting developments are also under way in America, and those who have had the largest personal experience in its use are most enthusiastic over its future application. The public may soon look to important publications from leading American authorities, who have had real experience in radium therapy. It is to be greatly regretted that, owing to the high price of the material, only three or four American surgeons have, so far as the Bureau of Mines is informed, been able to use it in quantities sufficient for the drawing of decisive conclusions. In the progress of the future applications of radium to the curing of disease, nothing is more to be feared than its use in nostrums of every kind. The "wonders of radium" have been so extensively exploited in the public press that already the name is being employed as a psychological agent in advertisements of all kinds of materials, many of which contain no radium at all, or, if this element is indeed present, in such small quantities that no therapeutic value can be expected. As bearing on the need of further experiment, attention is called to the fact that the concentrated action of large quantities of radium may effect cures that have been impossible with the smaller amounts heretofore available to the medical profession. It is doubtful if there is at the present time in the hands of the medical profession of America more than a single gram of this rare element, and the results of investigations soon to be published will show that the concentrated action of the gamma rays from several hundred milligrams arrest certain forms of cancer and other malignant growths when smaller quantities are without beneficial effect. It is highly important that the medical profession should also have some guarantee of the material they purchase, even if it is purchased in small quantities, and I am glad to note that the U. S. Bureau of Standards is preparing to standardize radium preparations. As severl frauds in the sale of radium have already been perpetrated upon American physicians, they should all require that the quality of the material purchased should be certified under conditions which prevent error.

In closing, I take pleasure in saying that I am authorized by the director of the Bureau of Mines to announce that a co-operative agreement has been entered into with the newly organized National Radium Institute, whereby the Bureau obtains the opportunity of a scientific and technological study of the mining and concentrating of carnotite ores and of the most efficient methods of obtaining radium, vanadium, and uranium therefrom, with a view to increased efficiency of production and the prevention of waste.

The National Radium Institute was recently incorporated with the following officers:

Howard A. Kelly, of Baltimore, President.

Curtis F. Burnam, of Baltimore, Vice-President.

Archibald Douglas, of New York, Secretary and Treasurer.

James Douglas, of New York, and E. J. Maloney, of Wilmington, as additional directors.

The Institute has no connection with the mining of pitchblende, details of which recently appeared in the Denver papers. It has, however, obtained the right to mine 27 claims in the Paradox Valley region, among which are some of the best mines in this richest radium-bearing region of the world. Nearly 100 tons of high-grade carnotite have already been procured. Under the agreement with the Bureau of Mines, the technical operations of the mines and mill are to be guided by the scientific staff of the Bureau. Work will begin in an experimental plant to be erected in Colorado, using entirely new methods developed at the Denver office of the Bureau of Mines. Concentration experiments also will be conducted in the Paradox, probably at the Long Park claims, and if successful will be applied to reducing the wastes that now take place. Within a year at most, the mill operations should make results certain and the extraction of ore and production of radium will then be continued on a larger scale. The separation of uranium and vanadium will also be studied, a contract having already been signed for all of these by-products that may be produced. All processes, details of apparatus and plant, and general information gained will be published for the benefit of the people.

The Institute is supplied with sufficient funds to carry out its plans.

The Institute has been formed for the special purpose of procuring enough radium to conduct extensive experiments in radium therapy with special reference to the curing of cancer. It also expects to carry on investigations regarding the physical characteristics and chemical effects of radium rays and hopes in time to be able to assist or perhaps even duplicate the effects of these rays by physical means.

Actual experience, especially of the Institute's President, in the application of the 650 milligrams of radium and 100 milligrams of meso-thorium already in his possession, have led him and his associates to believe that with larger supplies many of the variables that cannot now be controlled may be fully correlated, and that radium may become the most effective agent for the treatment of cancer and certain other malignant diseases. Important results have already been obtained by using high concentration of the gamma rays of radium with the alpha rays entirely cut off and the beta rays largely eliminated. Hospital facilities in both Baltimore and New York are already supplied.

The activities of the Institute are sure to be of benefit to the prospector and miner by providing a

greater demand for his already rare ore; to the plant operator by developing methods and by creating a larger market for his product; and to the people by assisting, and possibly by succeeding in controlling the most malignant of diseases. The radium produced is intended for the Institute's own use and will consequently remain at home.

The Bureau of Mines is especially fortunate in the opportunity to co-operate in the technological features of the work of the Institute.

THE WORK OF THE U. S. BUREAU OF STANDARDS IN METALS.*

By DR. G. K. BURGESS.†

First, a word as to the organization of the bureau and its methods of attacking problems of scientific and technical interest. For administrative purposes, and also for the greater convenience in dealing with the various routine and special problems here studied, the Bureau is divided into divisions each representing a portion of its work as classified according to the several branches of physical science and technology. There are thus the Weights and Measures Division, those of Heat, Electricity, Optics, Engineering with several large and important sections, and lastly that of Metallurgy and Metallography which was organized only last July by Director Stratton.

Metals Tests.—In metals, there is a great deal of testing done for various departments of the National government. By far the heaviest of this work for the government at the present time is chemical analysis, but oftentimes accompanied by physical tests, for the acceptance or rejection of material bought on specification. The greatest amount of this kind of work is done for the Isthmian Canal Commission and the Supervising Architect's office; and in addition to iron and steel commonly ranges over some 40 non-ferrous alloys and about 20 types of coated metals, including some 500 samples per year of various bronzes, brasses and white metals and several hundred samples of terne plate and galvanized iron. During the past fiscal year there were also 347 metallographic tests, including heat treatment, cooling curves, melting points and microscopic examinations. This routine work is extremely useful for serving as a basis for supplying data upon which to base specifications.

Rolled and Cast Brass Standards.—Regarding the work on non-ferrous, standard chemical samples, our chief chemist, Dr. W. F. Hillebrand, has prepared the following statement:

> The Bureau will soon issue a rolled brass carefully analyzed like its iron, steels and ores, for the purpose of checking analysis and their analytical methods. The preparation of a cast brass is also contemplated and, in fact, sample was prepared and nearly ready for analysis, when it was inadvertently spoiled in the process of mixing. This unfortunate accident emphasized most strongly one of the difficulties encountered in the preparation of satisfactory samples of materials of the nature of this particular brass and of all others that are subject to segregation in the casting. This brass, containing 5 per cent of lead, became very dark colored during the operation of mixing in the machine specially designed for the purpose of mixing metal chips, and it was found that the lead alone seemed to have undergone marked oxidation. The sample had to be discarded and will not be replaced until some method of castings is devised that will insure the requisite homogeneity without mixing. Possibly the method of com-

The experimental study now being made, in co-operation with a committee of this society, at the Pittsburgh laboratories of the bureau of the methods of casting bronzes and brasses with a view to determining and controlling the factors that influence the tensile strength of the casting, I mention here only for the sake of completeness, as this matter is presented in detail by the committee of which Mr. Clamer is chairman.

Some Investigations Under Way.—I will now pass briefly in review some of the work in metals that has been completed at the Bureau of Standards, and also mention investigations under way or to be taken up as soon as possible.

The specific resistance and temperature co-efficient of copper have been expermentally determined with great exactness and thoroughness, and the Bureau's results for these constants, which are of the greatest importance to the electrical industries, have been adopted not only by the interested technical societies in America, but are also recognized abroad as authoritative. Wire tables for cables based on these experiments have also been computed.

The ocular behavior of manganin wire resistance standards has been studied and the effect of moisture on their indications has been eliminated.

The radiation constants for a great number of metals have been determined at ordinary temperatures and some progress has been made on measurements of the spectral and total radiation of metals and oxides at high temperatures, including a study of the variations with temperature. This investigation has a very practical bearing in its application to the metallurgy of metals, the temperature of which it is desired to determine during any operation, since the corrections to apply to the various types of radiation and optical pyrometer when sighted on the several metals and oxides is determined from such radiation measurements.

A matter that has bothered the chemists a good deal is the loss in weight and deterioration of platinum crucibles and ware when heated. Some work has been done at the bureau in co-operation with a committee of the American Chemical Society and this is still in progress.

Allotropy of Iron.—A question that has been worrying metallographists for a quarter of a century is the allotropy of iron. We have just completed an investigation of the critical ranges A_2 and A_3 of pure iron using some fifteen samples from various sources. Besides the thermal study carried out by two methods

*Abstract of address before Institute of Metals, Chicago meeting, Oct. 14, 1913.
†Chief, Division of Metallurgy, U. S. Bureau of Standards.

with all the refinements at our disposal, this investigation has involved the preparation of very pure electrolytic iron at the Bureau and the remelting of the product to remove occluded gases. This remelting alone requires unusual precautions to keep the iron strictly free from contamination from crucible and atmosphere. The experience here gained will serve in the preparation of a series of iron-carbon alloys and special steels, the study of the equilibrium diagram of the former of which we have begun using materials absolutely free from all impurities. A thermal study of some commercial steels has already been completed in collaboration with Prof. Howe.

Railway Equipment.—Considerable attention is being given to the quality of the metals that enter into railway equipment and it is planned to greatly extend this work as means permit. At present there is cooperative work with the Pennsylvania railroad on the improvement of steel springs involving particularly methods of heat treatment and magnetic methods of testing Very promising results have been obtained, and I need hardly point out the advantages of a magnetic test of quality, in that the metal is not destroyed or changed in any way and the test nevertheless reaches throughout the interior of the mass of metal examined.

Work is being carried out on the segregation in steel ingots with particular reference to rails and for this we are using not only ingots made by American practice, but shall also be able to examine some English made ingots and in co-operation with one of the steel works have some of them rolled into rails which will also be examined as to quality.

Similarly in co-operation with several rolling mills, a preliminary survey of the American practice in finishing temperatures of rails is under way accompanied with a study in the laboratory of the properties of the rails.

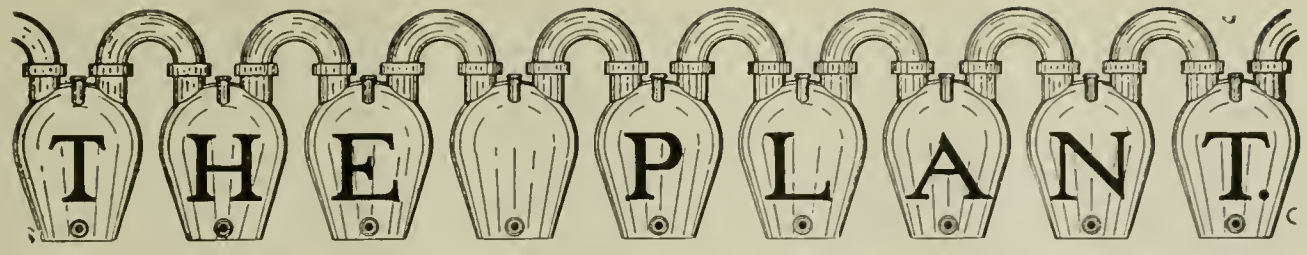
Railway car wheels are also to receive attention and a systematic study of the materials, properties, methods of manufacture, testing and service of chilled wheels is just being undertaken with the hearty support of the Interstate Commerce Commission, and the bureau is receiving the most cordial offers of assistance from all the railroads and car wheel makers who have been consulted thus far.

Heat Treatment Tests.—Among the investigations in metals of a general engineering interest may be mentioned a comparative study of methods of determining hardness, experiments on the relation between hardness and tensile strength of high carbon and alloy steels for different heat treatments and similar work for transverse and bending tests. In co-operation with the American Society of Civil Engineers, work has been begun on tests of a series of heavy H beams and strains in fire boxes have been studied for the Interstate Commerce Commission. The strains developed in structures of various types, by taking length measurements on members before and after erection, are also being studied on an extensive scale, including several large bridges such as the Oswego, Williamsburg and Kansas City, as well as high office buildings and the metal gates of the Panama Canal locks, with the object of comparing the actual with the computed strains.

Corrosion of Iron.—Investigations carried on by the Bureau of Standards for the past few years on the subject of the corrosion of iron have dealt primarily with problems growing out of electrolytic corrosion due to stray currents from street railways and other power sources. Self-corrosion proper has also been given some attention as well as the effects of sea water on reinforced concrete. A very complete series of researches has been carried on relating to phenomena occurring when electric currents pass through plain and reinforced concrete, and much light has been thrown on this hitherto little known subject. Investigations have been made into the fundamental laws governing electrolytic corrosion of iron, particularly when embedded in soil. The greater part of the work done by the Bureau of Standards has, however, had for its object the study of the prevention of corrosion of buried pipes, cables, structural steel in building foundations, etc., from damage due to stray currents. The work has comprised theoretical studies, experimental laboratory investigations and very comprehensive studies carried on in the field under actual conditions mainly in co-operation with several cities and public utility companies. A number of reports are now in preparation dealing with the various phases of the investigation.

There are three series of bureau publications: (1) Scientific papers, (2) Technologic papers, (3) Circulars of Information, any of which will be furnished on request. The last describe testing methods and serve the purpose of cutting down letter writing. A circular on "Metallographic Testing" has just been issued and one on "Testing of Materials," including metals, is in press.

The largest of the German gas engine companies reports $783,233 net profit for its trade year just ended, against $723,184 last year, and will again pay 9 per cent. The capital is $5,236,000. The turnover during the year amounted to $6,190,000, against $5,688,000 the previous 12 months. During the year considerable improvements were made in the old models, and several new models have been introduced. The heavy oil engine placed on the market has been well received. Extensions continue to be made and new plant laid down, and this policy will be continued. During the past year $302,000 was expended on new plant and machinery, against $440,000 the previous year. Wages continue to advance, the total increase per man per day since 1906 amounting to 45.16 per cent. The Vienna subsidiary was seriously affected by the Balkan war, and only made a net profit of $6,900.



MANUFACTURE AND USES OF HYDRATED LIME.

By H. E. BACHTENKIRCHER.*

The rejuvenation, or better, the entrance of technical interest and investigation into the lime industry, is another striking example of the impetus always afforded by the introduction of the scientist or as too often disparingly termed, theorist.

For the last decade or more, lime, as a building material, has been subjected to the rapid crossfire and assaults of Portland cement on one side and gypsum products on the other. And, in fact, up to a few years ago, things began to look very serious for the ancient and honorable business of lime burning; and every manufacturer of lime who wasn't threatened with immediate apoplexy, knew his final days would be spent in the poor-house.

However, as is usually the case, some manufacturers refused to be annihalated without a struggle and thereupon began to study the situation. It soon became apparent, that while lime (I am speaking here of quick lime, the oxide of calcium, the only commercial state of lime until recently) possessed desirable and unique properties for mortars, yet it was handicapped and being eliminated by also possessing other properties not so desirable, and which the construction would have outgrown. For instance, lime, when slacked and properly prepared, affords a colloidal-like paste or putty which has remarkable sand carrying capacity and at the same time remains very easy of manipulation by mechanics. Thus affording an ideal material for brick laying and plastering, because of rapid progress that can be made with it for these purposes, and hence extensively reducing the labor cost in masonry construction. Yet the care required in the preparation of ordinary lime for satisfactory mortars, offsets to a large extent its desirability; similarly with other properties of lime, until a resumé of the situation brought the investigators to these conclusions:

1. That lime, as then on the market, commercially, was not a finished product, as it needed quite a little preparation in the hands of the consumer, before it could be used.

2. From its chemical constitution, it was very perishable and possessed poor storage properties.

3. That the trend of the consuming trade in most directions, was for package preparations, rather than bulk or heavy cooperage, as then existing in the industry at that time.

Both of the competitors of lime in construction work, were packaged goods. Both were finished products, requiring little manipulation in the hands of the consumer; both possessed good storage features, but neither afforded the easy-working plastic mortars so desired in the trade.

With these conclusions in mind, it was easy to see that the biggest step toward the solution of the problem, lay in the development of a method of preparing lime at the plant, so the trade would be afforded an article requiring the minimum of manipulation on the job; in other words give the trade lime already slaked.

For a time many attempts and crude efforts at slacking lime were made, all following out the laborious methods of forming a paste or putty with water, then drying it and grinding to a fine powder.

A little experience soon taught the experimenters that the problem of drying slaked lime paste commercially was out of the question, hence practically no progress was made.

With the advent of more scientific investigation, which by this time had necessarily been introduced, it was not long before the fact was noted, that lime, calcium oxide, in combining chemically with water to form a hydrate, evolved a very considerable quantity of heat, and that this heat properly utilized could serve for the drying of the resultant hydrate, thus making the whole operation very cheap commercially. And from this fundamental principle, the manufacture of hydrated lime, as the product is known to the trade today, has made rapid strides.

Hydrated lime as on the market today, as most of you know, is a very fine white powder with a specific gravity varying from about 2.07 to 2.50, according to its magnesia content. It comes to the consumer packed in paper bags of 40-lb. weight and in jute bags of 100-lb. weight, and simply needs mixing with sufficient water to form a paste of desired consistency for the purpose at hand. All hand slaking with its annoyances and waste has been eliminated, thus accomplishing quite a material saving in labor as well.

It is not my purpose to go into the mechanical details of the methods which have been developed, for these have been satisfactorily solved in several different schemes; but rather to dwell on some chemical and physical features of hydrated lime, as produced today, which are handicapping the product especially

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in construction work. And which must be changed or overcome, before the rapid increase in consumption in this field is realized.

Commercial limes are of two general classes:

1. High calcium limes carrying usually 95 per cent or better of calcium oxide.

2. Dolomitc limes analyzing usually in the neighborhood of calcium oxide 55 to 56 percent, and magnesium oxide 42 to 43 per cent. Usually limestones run very high in magnesia or very low, but there are a few exceptions, however, in which the magnesia content is about 12 to 15 per cent. As yet, however, these limes are not being commercially hydrated.

Sketching briefly, the commercial preparation of hydrated lime consists in adding a definite quantity of water to a definite amount of lime, taking care that the quantities involved are in such relation that the chemical heat evolved will leave the resulting product a dry powder. Two methods are in most general use:

1. The Batch, in which approximately one ton of crushed lime is mixed with the required amount of water and a large mass of product produced at one operation.

2. The Continuous, developed by Mr. C. C. Rutzer of Chicago, in which as its name implies, the water and lime are mixed at such a rate and in such proportions, that a small constant rate of production ensues, the whole operation being continuous.

For the purpose of receiving more clearly the chemical and physical effects produced, a consideration of the Batch method will be better.

About the first feature established in hydrating dolomitc limes, was that the magnesia would not combine chemically with water under the conditions of commercial hydration. For invariably limes analyzing CaO 55 per cent, MgO 43 per cent, gave a combined water content of approximately 16 per cent, showing only the calcium oxide to be hydrated. With a high calcium lime analyzing around 96 per cent CaO the combined water content is always around 28 per cent, showing that all the available calcium oxide hydrates, while the reverse is true with magnesium oxide whether light burned or heavy burned.

In the amount of water evaporated during hydration, the rate of hydration—or the chemical combination of water and calcium oxide—plays a most important part. The rate of hydration, in turn, depends upon the degree of heat, and duration of burning to which the lime has been subjected, leaving aside the natural characteristics of the original limestone. The higher the temperature and the longer the exposure to temperature, the more the combination of the oxides with impurities, such as silica, aluminia and iron—and, what is more important, the less the porosity of the burned lime.

In general a rapid rate of hydration due to high porosity is desired, hence lime for hydration is usually burned rather quickly and at minimum temperatures.

Under actual operating conditions, it is found that the amount of water evaporated by the chemical reaction is about equal to that retained in chemical combination so that practically twice the amount of water necessary to combine with the calcium oxide present in the lime, must be added to insure complete hydration under atmospheric pressure. This union of calcium oxide and water, of course, is one of violence, for within 10 to 15 minutes a ton of lime previously crushed to ½ inch in size, is reduced to a fine, fluffy powder about 60 per cent of which will pass a 200-mesh screen, the remainder requiring but very slight grinding to complete its disintegration—that is all but the impurities and foreign matter. Almost by the time the water is all added, 1½ minutes, the mass is violently steaming and the temperature rises rapidly to 212° F. where it remains as long as water is being evaporated. As the evaporation ceases the temperature again rises due to the fact that chemical action is still going on, but there is no means of losing the heat mechanically, as calcium hydrate is a poor conductor, the loss by radiation and in cooling is slow. This second rise usually does not go beyond 230°, 235° when the temperature slowly falls as the mass begins to cool off. Hydrated lime while very warm, will run almost as freely as water and advantage is taken of this property, in subsequent operations at the mill.

Mechanically the problem has been quite simple, and it was supposed by everyone in the industry, that hydrated lime prepared in this fashion when wet up with water on the job, was identical with the older slaked putty—it is chemically but physically, not. The verdict of the bricklayer and plastered was that hydrated lime was "no good." And as the mechanics were universally of the same opinion, it was quite evident that there was a material difference between putty from dry hydrated lime and putty from quicklime mortar—box slaked.

Those of you who have any first hand knowledge of the average mechanic, realize he uses a language, picturesquely all his own in describing various properties of material with which he works, and while he understands exactly what he is trying to convey, yet an outsider can scarcely grasp it. But after learning the language it became evident that putty made from hydrated lime had lost much of its colloidal-like consistency, one property so desirable in lime mortars. The mechanics held that this was due to the lime becoming so hot in the process of hydration, that the product was burned. In slaking lime in the mortar-box, however, the large excess of water used kept the temperature down and the product was in *paste form* and never a dry powder, and no loss in plasticity was experienced. While in mortars from hydrated lime, this loss of colloidal-like consistency or plasticity, caused the mortar to work "lean," or "short" under the trowel; hence the amount of work done by the mechanic was limited, and a diminished amount of mortar is produced from a given quantity of hydrated lime, due to decreased sand-carrying capacity.

This realization was quite a serious blow, for the lime manufacturer was having enough troubles without stirring up new ones, and as this "short" or "lean" working property of hydrated lime has almost uniformly persisted, quite a set back to the development of the product as a construction material has been experienced.

It may be noted here, however that this short working feature of hydrated lime has not handicapped its rapid use as a waterproofing agent in concrete work. For it has been repeatedly demonstrated that a 10 per cent replacement of cement by hydrated lime, will not injure its strength, while the water absorption of the concrete is lowered about 65 per cent. This is due to a peculiarity of hydrated lime which will be noted later, that is of acting the part of a reversible colloid in presence of water.

Meanwhile the hydrated lime manufacturer has been more than encouraged by the new channels of trade his product has opened up, and in a large measure the handy labor-saving package feature of hydrated lime has been the determining factor.

For instance, in water-softening, when quick-lime with all its annoyances for the operation of softening had to be purchased, it was usually in small lots on account of its poor storage properties. Hence its price was higher with a consequent high cost per 1,000 gals. water softened. But now hydrated lime can be purchased in carloads with correspondingly lower price, and in addition the even weight packages permit of very close control, as little or no foreign matter is present. Hence exact amounts of lime can be added to the softener by almost any laborer.

Similarly in many kindred operations, where definite and at the same time small quantities of lime are desired, hydrated lime fills a long felt want and its market is widening every day.

The farmer, too, has realized the advantage of hydrated lime, and a large and constant consumption on the farm is being experienced, while in the great flour-mill centers, large quantities are used in freeing grain from "smut."

A new and novel use for hydrated lime came to my attention not long ago, at least it was new to me. For some time one of the firms with which I am connected had experienced a noticeable increase in demand for hydrated lime in a very rich dairy and creamery section. Thinking this increased use was due to more extensive white-washing and color-water painting and increased sanitary work in general, not much attention was paid to it. However, I received a communication from one of the salesmen asking whether our hydrated lime couldn't be made finer and the last traces of grit removed. I replied that it could but that I didn't see the necessity since the material as inspected by us was 87 per cent through 200 mesh. In due time an answer came back to me saying that my opinion might be all right, but the fact remained that the butter consumers dependent upon that section, were complaining of gritty butter, and that if we wanted to hold this new trade and increase it, our hydrated lime must be made finer.

An inquiry developed that quite a general practice of "sweetening" cream with hydrated lime prior to churning had arisen, and as near as could be learned was in this fashion: The acidity of the cream was determined and then a sufficient amount of hydrated lime (in this case a nearly pure calcium hydrate) for neutralization was added to the vat of cream. This hydrated lime was added in dry powder just as it came from the bags. Then the creams went to the churns and during this process the calcium salts formed were removed by solution and washing, leaving the finished butter nice and sweet. But unfortunately the slight percentage of grit in the hydrate wouldn't wash out of the "butter," hence the complaints by the consumer. My statement of the process may not be exact but it is as near as I could get at it, for the creameries were very secretive about the exact manipulation. At present we are trying to make what our mill men call "Extra Fine Talcum Powder" for this particular field, so that sweet butter without grit may be offered to the consumers in that section.

These with numerous other examples show the widening market which hydrated lime has developed for the lime manufacturer, so that along these chemical lines the demand for the product has been most satisfactory.

To go back to the deficiency of hydrated lime as a plastic material, as compared to old-fashioned lime-putty, let us see upon what property does plasticity or better, "easy-spreading" qualities of a lime paste depend.

As near as I have been able to determine, the plasticity of a lime paste is due to the firmness or strength of the suspension of calcium hydrate, or calcium hydrate and magnesium oxide in water, producing a colloidal-like emulsion, capable of more or less dilution without breaking. The more dilution this suspension will stand without breaking, or conversely, the more tenacious this suspension is at a given dilution, the more plastic the lime putty or mortar and the easier it is worked by the mechanic. Practically in a mortar the free water in this colloidal-like suspension acts as a lubricant in reducing the friction of the sand grains or other filler of the mortar, when it is spread. Now as all surfaces in building construction are more or less porous it follows, that mortar being applied once, these porous surfaces will be subjected to capillary attraction of varying intensity. Hence the water is pulled out of the mortar leaving it dry and stiff and hard to spread further, or "short working" as the mechanic calls it. If the water is so held in the mortar that it resists this "suction" as the mechanics call it, to quite an extent; or, (if the colloidal-like suspension formed in the putty has been quite stiff and stands good dilution, so that water may be given up to satisfy the capillary attraction and yet leave enough in the

mortar for lubrication—the mortar is "fat" and easy-working. But if the water is absorbed rapidly, leaving the material like so much damp sand on the mortared surface, the mortar is "short" or "lean" and hard-working. As far as the strength of the mortar is concerned, very little difference is noted between the tensile strength of a "fat" working mortar or a "short" mortar, provided the lime content is the same. What slight difference there is, is usually in favor of the "short working" mortar. But the supreme test of a mortar is whether it is "fat" or not, for if it isn't "fat" and "easy working" mechanics will be very slow to use it regardless of its properties in other directions.

In this connection the first observation noted was that dolomite limes upon dry hydration were invariably more plastic than pure high calcium limes undergoing the same process, while neither was as plastic when dry-hydrated as when slaked in the mortar box. This suggests that the loss of plasticity is in some way connected with the dry formation of calcium hydrate. For the magnesia not undergoing hydration apparently does not influence the change in properties, and practically it is observed that the loss of plasticity in hydrated lime is in a rough proportion to the calcium hydrate ratio.

An exhaustive microscopic examination of numerous samples of hydrated lime revealed the presence of quite a large percentage of refracting particles, which seemed to be more or less "crystalline hydrates," much shattered. With this discovery the problem seemed to be to make an amorphous calcium hydrate which would undoubtedly soak up water to a more tenacious suspension than a crystalline hydrate. But in this direction a decided "snag" has been encountered, for the nature of the reaction is such—a quick, lively, chemical one, and must remain so to be of commercial importance—that conditions for crystallization are almost ideal. In fact, much work has shown that it is almost impossible to produce dry calcium hydrate under any conditions and then reduce it to dry, separate, fine particles without having it largely crystalline. The same phenomenon holds true to a similar extent with the formation of calcium carbonate.

It has been observed, however, that the longer hydrated lime is soaked up with water the more plastic and tenacious the putty becomes, leading one to believe that the crystalline form gradually assumes an amorphous or more colloidal state in contact with water. But commercially on the job, this long soaking can't be utilized, for this would be getting back to the old mortar box method of slaking lime, which is just what the industry is striving to get away from. Consequently the hope of solution of this problem must lay in devising some means or method of causing this change to take place in a very short time after hydrated lime is mixed with water on the job. And here is the difficulty: How to induce a colloidal action under conditions that work for the precipitation of colloids.

In other words the difference between calcium hydrate prepared in the mortar-box from quick-lime, and calcium hydrate by dry hydration may be likened to that (if exact chemical consideration may be stretched a little) between *sol.* and *gel.*, the hydrated lime being the *gel.* And upon further consideration this rough analogy holds true also, for upon prolonged soaking with an excess of water, dry hydrated calcium hydrate slowly assumes the condition and properties of wet hydrated calcium hydrate—the *gel.* changes back to the *sol.* or the matured defloculaters, making a slowly reversible colloidal condition. And the problem thus narrows down finally to developing some means or perhaps of incorporating some defloculating agent to hasten this reversion.

In the late H. E. Ashley's work in the colloidal matter of clays, defloculation of the colloidal contents is accomplished by use of very small quantities of 100-lb. normal solution of alkalies and other compounds. The action resulting in a very fine, dilute and at the same time tenacious suspension, or solution. And this suspension or solution was invariably precipitated on addition of small quantities of the Alkaline Earth or their salts.

The conditions with hydrated lime therefore are just the reverse of Ashley's experiments, for our problem is to defloculate what is the precipitating agent ordinarily.

The use of alkalies as defloculating agents upon hydrated lime resulted in a still further loss of plasticity and in their presence, all colloidal like suspension was lost. So attention was turned to the employment of agents of an acid nature and so far our investigation with reference to the use of acid defloculating agents hold forth some promise, but nothing practical has been accomplished. However we have been able to induce this reversion and reassumption of colloidal properties sufficiently on a laboratory scale.

If dry hydrated calcium hydrate is mixed up with water to a putty and then ½ to ¾ per cent of sodium bicarbonate is added dry, the mass stirred and allowed to stand for 5 minutes, the entire paste or putty has assumed a gelatinous condition which is very tenacious. In fact all the colloidal properties of wet hydrated calcium hydrate are present and a most satisfactory mortar base is produced. This same reversion can be brought about by water containing dissolved CO_2, but not by CO_2 in combination with bivalent or higher bases, nor with normal monovalent salts, showing the free acid to be the agent.

This fact prevents this means of producing reversion from being of practical importance, for up to the present time no means has been devised for keeping a bicarbonate or free CO_2 in presence of a strong base like calcium hydrate, without chemical combination taking place. And as hydrated lime must be capable of being stored, at least six months, without much loss of

its properties, it is readily observed that this solution on a commercial scale, is out of the question.

Also very dilute solutions of sulphuric acid produce the same effect. Calcium sulphate, of course, is formed, and this acts as the defloculating agent. A stable agent and mixture here is afforded, but weather difficulty is encountered. A large portion of hydrate lime is used for white-coating plastered walls and for this purpose about ¾ hydrated lime and ¼ of stucco (the hemi-hydrated $CaSO_4$) is employed. This mixture should not set under 15 minutes to be of use practically. But with hydrated lime defloculated with H_2SO_4 the mixture sets in 7-8, hence it cannot be manipulated on the wall. This is due to the presence of hydrated $CaSO_4$ in the mass which sets up immediate crystallization of the hemi-hydrated calcium sulphate, so this defloculating agent is beyond our province as well.

But "meat in the cocoanut" so to speak has been located and though little progress has been made in finding a subtle defloculating agent, yet it is only a question of time and work.

The U. S. Consul at Hamburg, Germany, report that according to German experience hardwood is the best material for the production of high-grade flour, such as linoleum manufactures require, and this is turned out by machines some of which are recommended as rendering equally effective service with roots, branches, boughs, sticks, tender shrubbery, slabs, and wood waste of every kind. Reducing machinery of this character is used in preparing raw material for a good many chemical and other industries. The ordinary process of producing wood flour consists of feeding the material into a revolving iron cross beater. The material should be not larger than one-half or three-fourths of the length of a finger, and it is beaten to the desired fineness as sawdust in which is contained a large percentage of exceedingly fine meal. The capacity of the machine depends upon the fineness sought and the quality of the wood, brittlewood yielding a finer flour and a great quantity per hour than any other. When it is desired to obtain a meal finer than sawdust a rasping mill is employed. These rasping mills have an interior construction similar to that of the iron cross beater, a rasping disk revolving against the inner walls of the apparatus, the metal plates of which present rasping surfaces. Light material fed into this machine to be ground can not be ejected until it is perfectly ground, whereas in the machine first mentioned the iron cross beater merely revolves in the wood débris. When the output of flour sought is inconsiderable and time does not press, both an iron cross beater and the rasping apparatus can be utilized in the same machine.

The Viscosa Co., which runs a factory for the manufacture of artificial silk at Mytishi, near Moscow, has at the present time started the construction of another such factory in Finland.

FORMATION OF ALUMINUM NITRIDE FROM ALUMINA.*

By WALTER FRAENKEL.

CARBON AND NITROGEN.

The formation of aluminum nitride from aluminum and nitrogen or nitrogen compounds was first observed in 1862 by Briegleb and Geuther. (Ann. d. Chemie. u. Pharm. 123,238). In 1876 Mallet (Chem. News 33, 238; Lieb. Ann. 186, 155) made a more exact study of the reaction and since then it has been the subject of many researches. Of these only the work of Fr. Fichter (Zeit. anorg. Chemie 54, 322, 1907) will be mentioned here. The discoverers of the compound found that it evolved ammonia when it was treated with alkalies. The reaction, to be of technical value for the fixation of atmospheric nitrogen and the preparation of ammonia, must be based on the use of alumina and not of aluminum. Th. L. Willson was the first to use the reaction

$$Al_2O_3 + 3C + N_2 = 2AlN + 3CO$$

for the preparation of aluminum nitride and other nitrides "preferably in the electric arc" as the basis of his British patent No. 21755 (1895). (See also Mehner, D. R. P. 88999; British patent 12471 (1895). However, the first actual technical application of the reaction for the synthetic preparation of ammonia was made by O. Serpek and afterwards by the Societe Generale des Nitrures.

In the last few years Otto Serpek and others have done much work on nitrides. This literature has recently been collected by G. Coutagne: "Bibliographic Notes on the Nitride of Aluminum" (Abstract from La Houille Blanche), Grenoble, 1912. See also E. Donath ant A. Indra (The Oxidation of Ammonia to Nitric Acid: Stuttgart, 1913), have taken out a large number of patents, but we are still almost entirely without scientific data which the importance of the process makes desirable.

The objects of this investigation were:

(1) To study the influence of the temperature on the rapidity of the reaction and to determine the temperature at which the reaction takes place with marked rapidity.

(2) To determine the influence of nitrogen at different pressures.

(3) To determine the influence of carbon monoxide, when mixed with nitrogen, and to find equilibriums and the temperatures at which they exist.

(4) To find out the influence of different conditions and purities of the materials employed and to test the action of catalytic agents.

(5) To study the reduction of alumina by carbon when nitrogen is absent.

The investigations under No. 4 are not yet completed and will be published later.

*From The American Fertilizer.

APPARATUS AND METHODS.

To obtain the high temperatures necessary for the reaction, an electrically heated carbon tube furnace was used. The carbon tube was clamped between carefully bored graphite blocks. Strips of copper, to which the electric cables were attached, were fastened to the graphite blocks by means of strong iron plates which were bolted and screwed to the blocks. Between the graphite blocks the tube was surrounded by small pieces of charcoal which were covered by an asbestos jacket. This asbestos cover must be put on with care, to prevent the burning away of the charcoal.

A 10-kilowatt alternating transformer was used as the source of current. This was supplied from a primary circuit of 120 volts and 50, 25, 12.5, 6, 3 or 1 volt could be taken from its secondary at will. For heating the furnace 12.5 volts were used. The energy consumption varied somewhat with the condition of the tubes. Usually with 7 volts and 400 to 600 amperes, temperatures of 2,000° C. could be attained. The ends of the cables were cooled by winding them with lead pipe; through which water flowed, to prevent melting the solder. The regulation of the strength of the current was accomplished by placing two resistances, in parallel, in the primary circuit. The temperature could be accurately controlled and held constant for long periods. The ends of the carbon tubes were closed with double walled brass caps, through which water flowed. These were held in place with good shellac.

At the inlet end, where the carbon tube projected 120 m. m. from the graphite block, the shellac did not melt even when the furnace was at its highest heat; but the outlet end, where the tube only projected 30 m.m. from the block, a water-cooled lead tube was wound around the carbon tube to protect the shellac. These caps contained tubes for the gas inlet and outlet, and the cap at the inlet end was also provided with tubulus, covered with a little glass plate for taking the temperature readings with an optical pyrometer.

This furnace was found to be very satisfactory but it was not entirely impervious to gases. In general, the carbon tubes proved to be fairly gas-tight, for the outlet gases had approximately the same composition as the inlet gases, even when the tubes were heated. At the highest temperatures, however, a lively diffusion of gases, both in and out through the walls of the tube took place, for when nearly pure nitrogen was passed into the tube, the outflowing gases contained considerable carbon monoxide, some carbon dioxide and traces of oxygen.

This, at first did not appear to be of importance, for according to the patents carbon monoxide should have no influence on the results and at the temperature required for the reaction, in the presence of an excess of carbon, only carbon monoxide and nitrogen could exist. The results obtained, however, did not show sufficient agreement, even when the greatest care, in holding the temperature, etc., was used. They also varied markedly when different tubes or old and new tubes were used.

Finally, after a long series of experiments, this type of furnace was abandoned for exact measurements. The diffusion of carbon monoxide was greatly decreased by surrounding the carbon tube with a welded iron tube which was cemented to the graphite blocks with a waterglass-asbestos cement. This tube was filled with charcoal and nitrogen was passed through it during the heating of the furnace. However, a gas-tight furnace seemed less open to objections, especially when diminished pressure is desired and a definite atmosphere in the furnace is necessary.

A closed furnace, similar to that described by F. Fischer, was therefore constructed. It consists of a glass bulb, of about one liter capacity, which has two large and two small tubulated openings. Through the larger openings, which are fitted with rubber stoppers, pass brass cylinders which are closed at the ends with hard-soldered caps so that cooling water can be passed through them. To these the wires for conducting the current are soldered. The inner ends of the brass cylinders are fitted into holes drilled in larger graphite cylinders, which are coated with an electrolytic deposit of copper. The inner ends of the graphite cylinders are connected by a thin carbon tube which is heated by the current. Good contact between this carbon tube and the graphite cylinders is assured by placing a thin copper cap over each end of the carbon tube. This prevents the formation of arcs, which might readily decompose the charge or the products of the desired reaction.

A T tube is fastened to one of the smaller tubulated openings by a ground glass joint. The outer end of the T tube is closed with a small glass plate, through which the temperature of the carbon tube can be taken with the pyrometer. The side tube of the T tube is provided with a glass stopcock. The other smaller tubulated opening into the furnace serves as the gas inlet. During the runs the whole apparatus was placed in a trough of running water to prevent heating and cracking the bulb.

The dimensions of the furnace are as follows:

Diameter of the bulb	120 mm.	
Length of the larger tabulated openings	100 mm.	Diameter, 20 mm.
Length of the graphite cylinders	98 mm.	Diameter, 30 mm.
Length of the brass cylinders	120 mm.	Diameter, 20 mm.
Length of the carbon heating tube	96 mm.	Outside dia., 10 mm.
Thickness of wall	1 mm.	

To obtain a temperature of 1,500° C. it was necessary to use between 15 and 17 volts and about 100 amperes (25 volts were taken from the transformer; resistance used in the primary circuit). The temperature required could be reached very quickly and, if the contacts were good, it remained very constant. After shutting off the current the temperature in the

furnace falls so rapidly that accurate determinations of length of time of heating can be made.

The only objection to this furnace is the small dimensions of the carbon tube, which allows the use of only 0.5 to 1 gram of charge in each experiment. A third furnace has been built, which will allow the use of larger amounts of material. It was not used for any of the experiments of this series.

The materials used in the experiments were pure alumina, such as is used in the electrolytic preparation of aluminum containing only traces of alkali, and lampblack (soot) obtained by decomposing acetylene. This carbon is very pure and very fine and was heated to bright redness before it was mixed with the alumina. The mixture ordinarily used contained 2 alumina to 1 carbon. This gives a considerable excess of carbon, for the theory requires for 2 alumina only .72 carbon. To give an absolutely intimate mixture of the substances they were ground together until a homogenous dark mass was obtained. The mass was then usually pressed into little cakes (for use in furnace II this was always done), and then broken up into small pieces and placed in the carbon tube. To hold the charge in place and to prevent it from sliding into the cooler part of the tube small plugs of cotton were used.

The nitrogen content of the products was determined by boiling for a long time with concentrated potassium hydroxide, and passing the ammonia evolved into standard hydrochloric acid. This simple process gave much more satisfactory results than treatment with alkali, after previous decomposition of the substance with pure sulphuric acid.

THE MEASUREMENT OF TEMPERATURE.

The temperatures were measured with a calibrated Holborn-Kurlbaum optical pyrometer. A comparison of this instrument with a Wanner pyrometer showed only unimportant differences which would not affect the accuracy of the measurements. The standard lamp was also compared, from time to time, with another calibrated lamp, but no differences worthy of note were observed.

Only the temperature measurements which were made in furnace II are given in detail in the following experimental data. Sighting at the outside surface of the tube was not sufficient, for it was the temperature on the inside of the tube that was desired. If the small carbon tube was sawed throughout its length, so that a slit one mm. broad was formed, this slit appeared as a brighter line on a bright background and the measurements were very satisfactory. But this method was not sufficiently exact, particularly when the surface of the charge and not the back wall of the tube was sighted on. On the contrary, temperature measurement through a small hole in the tube is exact.

In order to make sure of the relation between these two methods of observing the temperatures, the furnace was changed so that observations of the inside of the tube could be made laterally through a hole which had been bored in a graphite electrode. It was found that if a diaphragm, containing a small hole, was placed in the hottest part of the carbon tube and the temperature was measured through this hole by means of the bored-out electrode, the measurement agreed exactly with the temperature taken through a hole in the carbon tube through the regular sighting tube of the furnace. This was black body radiation which is necessary in optical pyrometry.

Table No. 1 shows the differences obtained by the different methods of measurements. When the temperature was measured through the slit, the results were from 50° to 60° too low. If the back wall of the tube was sighted through the slit, the readings agreed well with those taken through the hole. (The relation of nitrogen content to temperature changes at about 1,500° is very close). These measurements were substantiated by measurements taken from the side, at the hottest point, and were surely made with black body radiations. Since substances, which do not give black body radiations, always have higher temperatures than the optical pyrometer indicates, the results in the table, which show the lowest nitrogen content, must have been attained with correct temperature readings.

TABLE I.—TEMPERATURE MEASUREMENTS—TIME OF HEATING, 30 MIN.—TEMPERATURE, 1,500° C. ATMOSPHERIC PRESSURE.

No.	Nitrogen content.	Method of sighting.
7	21.29	slit
12	22.87	slit
8	7.11	hole
9	8.35	hole
13	6.87	slit. The point sighted on was free of charge.
14	4.69	

Optical temperature measurements, made by sighting through a small hole in a dark surface, may be very incorrect. It is much more exact to sight through a small hole in a bright field. The instrument can then be sighted on the bright surface and the greater brightness of the hole gives a more accurate determination. In cases where the hole is very small, temperature readings may be 20 to 30 degrees in error. Different observers may vary markedly in their readings; the amount of light in the laboratory is not without influence and finally the fatigue of the observer must be taken into consideration.

THE RAPIDITY OF THE REACTION AT DIFFERENT TEMPERATURES.

The question of the amount of nitrogen that can be fixed at different temperatures and in different lengths of time is of both special and technical interest and is discussed in many patents. Donath and Indra (l. c., p. 42), without stating the source, give the following data as operating results obtained by the Societe Generale des Nitrures: About 18 per cent of nitrogen was fixed in 2 hours at 1,500° C.; the same amount in 1½ hours at 1,600° C; 25 per cent in ¾ of an hour at 1,700 C, and from 30 to 35 per cent in 20 minutes at 1,750° C. These data were obtained with pure

alumina and pure carbon. (If these figures are correct, they must have been obtained with the carbon in the form of a very fine powder—lampblack or graphite).

The results of our experiments are shown in table No. 2. They were obtained in furnace II by heating the mixture for half an hour at the temperatures given. The reagents used were mixed as before, i. e., 2 alumina to 1 carbon. The nitrogen used was from a cylinder under pressure. It was purified by passing it through a tube 30 cm. long filled with reduced copper (pieces, wire and powder) which was heated to low redness, and dried by passing it through sulphuric acid. About 5 cc. of the gas passed through the apparatus per minute.

As will be seen from an examination of the table the fixation of nitrogen at 1,350° C. is very slight, at about 1,500° C. fairly rapid and above 1,500° C. it increases with extraordinary rapidity. It is beyond question evident that at high rates of transfer the determination of yields, made after a definite time of contact, no longer gives a comparable measure of the speed of reaction. (With a 2 to 1 mixture the reaction should yield a nitrogen content of 28 per cent). The value given for 1,550° C., approximately 20 per cent, is already somewhat high for comparison with the other figures.

TABLE II.—THE REACTION AT DIFFERENT TEMPERATURES—TIME OF HEATING, 30 MINUTES.

No.	Temp. deg. C.	Per cent of N. in the product.	Mean.	Remarks.
23	1350	0.2		
19	1400	3.48	3.1	
75	1400	2.65		
72	1450	3.17		
73	1450	4.01	4.4	
24	1450	6.09		
39	1450	4.27		
8	1500	7.11		
9	1500	8.35		No. 14 tube, with slit
13	1500	6.87		in the middle: With-
14	1500	4.69	8.0	out charge.
15	1500	7.57		Nos. 47 and 60: Nit-
45	1500	8.39		rogen purified with
47	1500	10.22		especial care.
60	1500	9.64		
21	1550	22.34		
43	1550	16.29	19.5	
46	1550	22.34		
18	1600	26.36		
44	1600	23.51	24.5	
46a	1600	23.46		

The experiments show that at 1,500° C. the yields are still proportional to the time. While the mean of the results for half-hour amounts to 8 per cent, two experiments (Nos. 17 and 38) showed after 1 hour 14.22 and 15.03 per cent. One experiment No. 6, gave only 22.7 per cent N_2 after 1 hour at 1,550° C., while the mean for half hour was 19.5 per cent.

As for the results obtained from single experiments, the differences found in those run at the same temperature should not be assigned too much importance. It must be remembered that slight differences in the temperature around 1,500° C. cause great changes in the amount of nitrogen fixation and that the measurement of temperatures is only subjective. The mean values, in all cases, give a sufficient degree of accuracy. The use of nitrogen, which was freed from oxygen with especial care by passing it through a porcelain tube about 70 m.m. long heated electrically to between 700° C. and 800° C., appeared to give slightly higher results (No. 47 and 60).

Since carbon monoxide is one of the products of the reaction, the reaction does not take place in pure nitrogen, but in an atmosphere of carbon monoxide and nitrogen. It was found that the gases leaving the furnace, when a temperature of 1,500° was employed, contained about 4 per cent of CO (volume of gases about 50 c. c. per minute). This ratio, in one experiment, remained practically constant for one hour, thus confirming our previous statement that during this time the reaction proceeds with constant rapidity. At 1,550° C. the gases contained a fairly constant amount of CO of 5 per cent, while at 1,600° C. the CO content was at first over 6 per cent, and after 20 minutes it decreased to 3 per cent. This proves that at 1,600° C. the reaction is at first very rapid and then slows down markedly. The influence of carbon monoxide will be considered at length in a later chapter.

As regards the results obtained in the large furnace I, a maximum value of 22 per cent was obtained by heating for one hour at a temperature of 1,600° C., which agrees fairly well with the average of those obtained in furnace II. Further experiments with furnace I will be carried through later.

THE INFLUENCE OF THE NITROGEN PRESSURE.

An American patent (No. 1,031,581-82) granted to S. Peacock and the E. I. duPont de Nemours Powder Co., is based on the absorption of nitrogen by a mixture of alumina and carbon under diminished nitrogen pressure. The reaction given is

$$Al_2O_3 + 6C + 3N_2 = Al_2C_3N_6 + 3CO$$

This compound, $Al_2C_3N_6$, containing about 48 per cent of N_2, should give ammonia with steam. A mixture of 3 parts of alumina and 2.4 parts of carbon was used, with the nitrogen under 500 mm. of mercury and a temperature of 1,500° C. Such a mixture should give, according to the Peacock formula, a yield of 46 per cent, but in the ordinary course of the runs only 22 per cent was obtained.

TABLE III.—INFLUENCE OF THE NITROGEN PRESSURE.

No.	N. Press. mm. Hg.	Alumina.	Carbon.	Time of heating.	Temp.	Per cent N. in Res.	Remarks.
6	1 Atm.	2	1.0	60 min.	ca. 1550°	22.66	Test run.
1	ca. 500	3	2.4	60 min.	ca. 1550°	19.0	
2	ca. 150	3	2.4	60 min.	ca. 1550°	19.4	Slit closed by sublimate cont.
4	ca. 100	3	2.4	60 min.	ca. 1410°	1.37	AlN and Al_4C_3.
5	250-300	2	1.0	60 min.	ca. 1550°	26.26	Temp. not very constant.
30	ca. 350	2	1.0	30 min.	1550°	8.67	
	1 Atm.	2	1.0	30 min.	1550°	8.0	Mean of results in Table 2.

Temperatures marked *ca.* were read through the slit and had to be corrected by the addition of +50°.

Our experiments were carried out with the gas passing through the apparatus and the results are given in Table No. 3. They show that a diminished nitrogen pressure of not only 500 mm. but as low as 150 mm. allows the fixation of a high percentage of nitrogen. This fixation is not limited, however, to a 3 to 2.4 mixture for the usual mixture of 2 to 1 at reduced pressures and at atmospheric pressure shows at least as good results. In comparing the results obtained from the 3 to 2.4 mixture with those obtained from the 2 to 1 mixture, it is seen that the yields in experiments 1, 2, 5 and 6 are quite high and that they correspond much better with results obtained with the ordinary reaction as a basis than they do with the Peacock reaction as a basis, which latter should give a much higher fixation of nitrogen. These experiments do not show the slightest indication that the reaction takes place according to the Peacock equation, which from the first appeared quite improbable. Stronger proof can only be obtained by the examination of the decomposition products.

THE REACTION IN A CARBON MONOXIDE-NITROGEN ATMOSPHERE AND THE EQUILIBRIUM.

As seen in the last chapter, the lowering of the pressure of the nitrogen has only a slight influence on the speed of the reaction, when the diminished pressure of the nitrogen is brought about by a partial exhaustion of the whole apparatus. Quite a different result can be obtained when the partial pressure of the nitrogen is lowered by mixing it with other gases, and especially when carbon monoxide, the gas produced by the reaction, is used.

If the reaction

$$Al_2O_3+3C+N_2=2AlN+3CO$$

is considered as reversible, conditions of equilibrium are shown under the supposition that Al_2O_3, C and AlN are components, and are thus phases of constant composition. The gas phase consists only of N_2 and CO and at constant pressure and constant at the concentration of N_2 and CO must be determinable, i. e.,

$$\frac{Cn_2}{Cco_3} = K$$

If more CO is present than corresponds to this relation, the reaction must proceed from right to left, i. e., the aluminum nitride present must burn in the carbon monoxide to aluminum oxide, carbon and nitrogen. If the reaction continues sufficiently long the change must be complete. If the concentration of the carbon monoxide is held at some chosen point below the equilibrium concentration, complete change to the nitride must also take place. On approaching the equilibrium concentration it is probable that the speed of reaction, in either direction, will diminish. The experiments, which were carried out in furnace II prove this.

The substances containing nitrogen, used in this series, were prepared in furnace I. In order to avoid the mistake, due to the burning of AlN in oxygen, that the reaction proceeded from right to left, the nitrogen was purified with especial care. As has already been mentioned, the gas was pasesd through a porcelain tube filled with reduced copper and heated by electricity to about 700° C. It was then passed through a large U tube which was filled with soda-lime to remove carbon dioxide. No oxygen could be found in this gas with a Bunte burette. Alkaline pyrogallol, however, became faintly colored after long standing in contact with the gas, indicating a trace of oxygen.

When it is considered that the gas, before reaching the charge, must pass through the red-hot carbon tube, it must be admitted that this trace of oxygen could not affect the results. The gases were mixed in a gasometer. The carbon monoxide was prepared from formic acid. It was free from CO_2 and contained

TABLE IV.—MIXTURE OF CARBON MONOXIDE AND NITROGEN—EQUILIBRIUM.

No.	Vol. per cent CO.	Nitrogen cont before	after	Time of heating min.	Remarks.
		Temperature 1500°.			
	4.0	0	8.0	30	Average.
70	11.0	0	3.15	30	
65	11.0	0	4.81	30	
53	19.0	7.34	7.83	30	
54	19.0	7.34	8.17	30	
55	21.0	0	0.9	60	
(50)	23.0	7.5	6.9	30	Incorrect.
51	23.0	7.5	9.0	30	
41	37.5	0	0	30	
49	43.5	11.21	10.28	30	
48	50.0	11.21	9.44	30	
36	53.0	26.4	23.5	30	No. 35: Traces of moisture in furnace.
35	53.0	26.4	22.4	30	
74	98.0	12.8	9.6	30	
		Temperature 1600°			
71	25.0	0	16.10	30	
68	34.0	0	12.73	30	
57	47.0	0	6.98	30	
61	47.0	0	2.16	30	No. 61: Temp. a little high during part of run.
62	47.0	0	1.58	30	
56	67.0	0	0	30	
59	69.0	1.8	0	60	
76	98.0	12.8	11.7	30	
27	98.0	19.49	12.96	30	
52		22.6	15.95	30	
		Temperature 1700°			
63	70.0	0	11.6	20	Temperature measurement uncertain. Sight hole covered by sublimate.
64	70.0	0	10.1	20	

about 98 per cent of C. O. Experiments were run at 1,500°, 1,600°, and in two cases at 1,700° C. and under atmospheric pressure. Where the substances, prepared in furnace I, containing nitrogen were not used the usual mixture was employed.

As has already been mentioned, the experiments in which pure nitrogen was used really took place in an atmosphere containing, at 1,500°, about 4 per cent of CO by volume. In order to determine the amount of CO set free by the reaction, samples of the outgoing gases were taken every 15 minutes. Practically no change occurred in the composition of the gases, however, for in this series of experiments the composition of the charge did not change appreciably. Also, in these experiments the gas was passed through the apparatus very rapidly (1 c. c. per second). The results are given in Table No. 4. They show that at

1,500 a small increase in the percentage of CO slows down the reaction appreciable, that at 20 per cent the reaction almost ceases, and at 37 per cent nitrogen is no longer fixed.

Three of the experiments, made on substances containing nitrogen (Nos. 53, 54 and 51) with about 20 per cent of CO, show a slight increase in nitrogen content, while No. 50 for some unknown reason shows a decrease in nitrogen. As an experiment made under these conditions with the ordinary mixture shows a nitrogen increase, experiment No. 50 should be disregarded. The CO concentration and the equilibrium are closely related; the equilibrium shifting, as we shall see later, toward a lower CO concentration as the temperature falls. In these experiments the temperature may have been somewhat too low and therefore have passed the equilibrium limit. In pure CO the nitrogen content becomes markedly less, at 50 per cent CO the loss is not nearly so great, while at 43 per cent CO it is very small. At 1,600° a similar relation is noted, but the equilibrium concentration shifts very plainly toward a higher CO concentration.

While these experiments show the existence of an equilibrium, they do not determine its exact location. It must be explicitly understood that its position can, at present, be only approximated, for not enough experiments have been made and the results of parallel experiments sometimes show such marked differences, that it is not certain whether the percentage of nitrogen lost by the substances in the different experiments furnishes a reliable measure of the speed of the reaction. Slight changes in temperature may also cause marked differences in the reaction near the equilibrium point. It is plainly evident from a study of the data that, at a pressure of one atmosphere, the equilibrium concentration lies between 25 and 40 per cent of CO at 1,500° C. and at 1,600° C. it lies between 50 and 65 per cent CO. That it shifts, with rising temperature, toward a higher content of CO is shown by the two experiments made at 1,700° C., where, with 70 per cent of CO present, a rapid rate of fixation of nitrogen took place.

These results should be interesting to the technologist. If generator gas is to be used, it must be at higher temperatures, for it is useless to expect any reaction acceleration near 1,500° C., with a gas containing as much carbon monoxide as generator gas. In other words, the higher the temperature the less the purity of the nitrogen affects the reaction.

These experiments also show why the results obtained with the furnace I could not be duplicated. The charge was surrounded by an atmosphere which contained more or less CO according to the porosity of the carbon tube. The gases often contained as much as 15 per cent CO. The results obtained at about 1,500° C. must therefore have varied. This also explains why the nitrogen content of the product became lower the longer a tube was in use and also why, in spite of the protecting layer of charcoal, the charge was attacked by atmospheric oxygen.

The shifting of the equilibrium with the temperature indicates that the reaction by which AlN is formed is endothermic. The only thermochemical data that exists on the heat of combustion of AlN to Al_2O_3 and N_2 were obtained in a bomb calorimeter by Konstam for Fichter (l. c.), but the results are not exact for the AlN was not burned quantitatively. The value, + 166,000 calories per gram molecule represents, therefore, only a low limit.

If we reverse the reaction

$$2AlN+3CO=Al_2O_3+3C+N_2$$

then

$$2AlN+O_3=Al_2O_3+N_2+2.166{,}000 \text{ cal.}$$

(Fichter) and

$$3CO=3C+O_3-3(26{,}300+3{,}350) \text{ cal.}$$

by addition gives us

$$Al_2O_3+3C+N_2=2AlN+3CO\text{—about } 243{,}000 \text{ cal.}$$

In the above equations the 26,300 cal. is derived from the heat of combustion of the diamond to CO (Pollitzer: The Calculation of Chemical Affinities by the Nernst Heat Theorum, p. 161, Stuttgart, 1912). and the 3,350 cal. from heat of formation of the diamond from carbon. Therefore the reaction by which AlN is formed from Al_2O_3, amorphous carbon and nitrogen is, indeed, strongly endothermic.

The calculations of the heat summation from the equilibrium data according to van't Hoff and Nernst, and also on the equilibrium concentrations at other temperatures will be published later.

THE INFLUENCE OF DIFFERENT FORMS OF MATERIAL USED IN THE CHARGE, AND OF DIFFERENT CATALYTIC AGENTS.

These investigations are not yet completed and the results obtained will be published later. It is known, however, that different kinds of carbon (soot, coke, graphite and charcoal) show a marked difference in the speed of reaction.

It can further be stated that so far no indications have pointed to any marked change in the speed of reaction at temperatures about 1,500° C. when one of the catalytic agents most frequently mentioned in the patents is used.

THE REDUCTION OF ALUMINA BY CARBON.

Finally it will be interesting to know whether any marked reduction of alumina by carbon takes place, when nitrogen is absent, at the temperatures at which the nitride is formed. From previous investigations this did not seem very probable, for much higher temperatures have always been employed. P. Askensay and A. Lebedeff (Zeit. Elektrochem. 16, 559 (1910). See also literature) deny that a temperature nearly as high as that of the arc is required for the reduction and state that the reduction takes place at about the sintering point, i. e., 1,900° C.

Our experiments were made in furnace II either in a vacuum or under diminished pressure in an atmo-

sphere of carbon monoxide. With the vacuum obtained with water suction pump (20 mm. of mercury pressure) there was from the very beginning of the experiment an atmosphere of carbon monoxide, for the atmospheric oxygen was changed by the carbon to carbon monoxide and through the carbide formed (see later) the nitrogen was combined as AlN.

We had hoped to be able to recognize the beginnig of the reduction by the rise in the manometer due to the formation of carbon monoxide and by taking the temperature at this time to find the exact temperature at which marked reduction begins. An obstacle was, however, encountered to simultaneous temperature and pressure measurements. It was found that at or only slightly above 1,500° C. the hole or slit in the carbon tube was closed by sublimed substances and that the outside of the tube was also covered with sublimate.

It was found necessary to make a determination of the voltage and amperage which would produce a temperature of 1,500° C. with the tube empty and then to use the same figures in making an actual run. If the contracts were not good slight changes in the temperatures would ensue and the experiments were rendered somewhat unreliable. This uncertainty could, however, be minimized by exact determinations of the relation between the temperature and the electric energy during the period before sublimation began.

The agreement between the readings in the preliminary runs and the actual determinations was very good. Although the temperature measurements were made, in part, through the slit, they seem to have been reasonably exact for they were made on the wall of the tube. The substances, after being well mixed (2 parts of alumina to 1 part of acetylene soot) were heated to 1,400° C. and then pressed into little cakes. About ½ gram of this mixture was used. As has already been mentioned, the slit was closed by sublimed substance at or only slightly about 1,500° C. (The evolution of gases was plainly indicated by the manometer at the same time).

This sublimate was found, on examination, to consist mostly of aluminum carbide, so that about 1,500° C., at the temperature where the formation of aluminum nitride takes place with rapidity, alumina is reduced by carbon. This leads to the conclusion that the formation of aluminum nitride follows the formation of the carbide.

Other interesting facts were learned from the experiments. For example, if the temperature was maintained at or only a little above 1,500° C. and the heating was continued for about 40 minutes, the little cakes of charge held their form and the slit was closed by a sublimate of fine, needle-like substance just above the charge. An analysis showed that while the charge contained only a little aluminum carbide, the sublimed substance contained about 50 per cent carbide. The analysis was made by decomposing the carbides with acid and determining the methane set free. (See Askensay and Lebedeff, l. c.). Hydrogen was not detected in the gas evolved.

The product of the reaction was also analyzed for carbide, but too much weight cannot be placed on the results of the analysis, for the product, as has just been shown, consists of two parts, whose relative proportions depend on uncontrollable conditions. In many of the experiments the carbide content in the reaction product was in the neighborhood of 10 per cent (in No. 21 it was 15.7 per cent). It is self-evident that this carbide would give, with nitrogen, a quantitative yield of aluminum nitride. Calculating this carbide to the nitride shows a nitrogen content of about 6 per cent, an amount which agrees very well with the results obtained in the nitrogen fixation experiments. At a temperature of about 1,600° C. sublimation was very rapid. At this temperature carbide, which was easily recognized by its yellow color, was found in all parts of the tube.

Experiments carried out at 1,525° C. to 1,550° C. and at a pressure of 60 mm. of mercury (the apparatus was previously filled with CO) also produced a sublimate of Al_4C_3. This pressure of CO is about the same as its partial pressure in a gas mixture containing 92 per cent by volume and 8 per cent of CO. The formation of a sublimate was also observed at 1,700° C. and 70 per cent of CO and in one experiment under very low nitrogen pressure (see Table No. 3, No. 2). At 1,700° C. the sublimate substance contained scarcely any carbide. In experiment No. 2 both carbide and nitride were present.

When a sublimate was formed, a considerable content of carbide was indicated. If no sublimate was found, treatment of the reaction product produced very little evolution of gas. Why sublimation generally takes place is not known with certainty. It may be that the carbide is volatile at the temperatures used and that it sublimes soon after it is formed, to a cooler place. Or it may be that the alumina itself is volatile at these temperatures and that the vapor reacts more easily with carbon. In support of the latter idea is the fact that the carbide always forms a thick layer near the hole or slit in the carbon tube and that under the microscope, sublimed alumina is seen with the carbide. In those cases where, in spite of the presence of nitrogen, a sublimate was produced, it must be concluded that the speed of sublimation exceeds the speed of carbide formation, which latter is reduced here by the strongly diminished partial pressure of the nitrogen and the presence of carbon monoxide. From these experiments it seems probable that the aluminum carbide in the sublimate is changed, after it is formed, wholly or partially to the nitride.

CONCLUSIONS.

The main conclusions from the foregoing investigation are:

(1) The formation of AlN from alumina, carbon

and nitrogen begins, when very fine carbon is used, below 1,400° C. and is very brisk above 1,500° C.

(2) The reaction proceeds with approximately the same speed, whether under atmospheric pressure or at a diminished pressure as low as 250 mm. of mercury.

(3) Carbon monoxide lessens the rapidity of the formation of the nitride. With 25 to 40 per cent by volume of CO, and equilibrium is established at 1,500° C. and a pressure of one atmosphere, and at 1,600° C. when the volume per cent of CO lies between 50 and 65.

(4) Alumina is reduced to Al_4C_3 with marked rapidity by carbon, in an atmosphere of carbon monoxide, at a temperature just above 1,500° C. and under a pressure of 20 to 65 mm. of mercury.

(5) With different kinds of carbon the reaction takes place with varying rapidities.

A process for converting petroleum into gasoline, is described in a recent issue of the London *Times Engineering Supplement*. In this process, which depends on catalytic action, the petroleum is placed in a high still having a conical bottom passing through the fire bars. A continuous feed of petroleum and of hydrogen under pressure is passed into the still from the bottom, and contained in the still is the nickel used in Normann's process for hydrogenating oleic acid. Strong agitation is maintained by means of a stirrer in the still, the latter being heated to a little above the temperature at which gasoline or whatever hydrocarbon is wanted becomes a gas. The vapors of gasoline or other light hydrocarbon, as the case may be, are carried up by the hydrogen and the heavier hydrocarbons mechanically carried up are condensed in the upper part of the still and fall down, while the light vapors, with the hydrogen, are passed to the condenser. The hydrogen from the condenser is returned to the still. The petroleum, a saturated compound, is thus split up into a saturated hydrocarbon, say, gasoline, and a heavier unsaturated hydrocarbon; the latter, it is claimed, at once takes up hydrogen in the presence of the catalyst, and becomes saturated, when it is again broken up into gasoline and an unsaturated hydrocarbon, which is again hydrogenated. The process is continued until the nickel becomes inactive and the petroleum in the still becomes overloaded with tarry matters. The tarry compounds and the nickel are then removed, and the latter is regenerated. The method is controlled by Messrs. Planes, Ltd., of Birkenhead, England.

Inquiry is made regarding the price at which pig iron can be furnished by the Hanyang Iron & Steel Works. The company states that for local sales of foundry pig iron in Hankow, China, it is receiving 33.50 Hankow taels ($22.52 U. S. gold at present quarterly exchange rate of $0.669) per ton ex works.

SLUDGE ASPHALTUM FROM THE TREATMENT OF CRUDE MINERAL OILS.*

By F. C. THIELE.

Since the discovery and commercial development of the immense oil deposits in the mid-continent, principally in Oklahoma, Northern Texas, Kansas and Northern Louisiana, a large refining industry of these oils rapidly developed. At first only skimming plants were erected, in which the oil was separated into benzine and some illuminating oil, while the balance was sold as fuel oil. In the course of time, however, complete refineries came into existence, in which the crude oil was refined completely and divided into the different commercial products. The Oklahoma crude petroleum has the following average composition:

	Degrees C.	Specific gravity.	Per cent.
Naphtha	161.2-225.5	0.7107-0.7550	14.46
Burning oil	225.5-332	0.7550-0.8480	32.73
Gas and lubricating oil	322 -326.6	0.8480-0.8733	11.60
Wax and lubricating oil	326.6-326.6	0.8733-0.9055	20.30
Residue in the still			17.91
Gas and loss			3.00
			100.00

The distillation of the crude oil was conducted with the aid of dry steam in order to protect the distillates against pyrogene decomposition during the run.

As the Oklahoma crude oil, like nearly all Western crudes, contains asphaltum (about 4 per cent), it is impossible to manufacture cylinder oils directly from the crude oil. After experimenting for some time the refiners finally decided to subject the crude oil to a treatment with sulphuric acid to remove the asphaltic compounds and dark-colored hydrocarbons. The oil is for this purpose mixed in agitators with sulphuric acid, specific gravity 1.835, usually forty pounds of acid being required for forty-two gallons of crude oil. The oil and acid are agitated until the acid tar separates from the oil, leaving the latter clear. At this stage the compressed air, which was employed as the mixing agent, is stopped and the sludge tar is allowed to settle. It is then drawn off the bottom of the agitator, while the clear oil, after neutralizing with an alkali and washing with water, is ready for distillation. The loss of the crude oil by this treatment amounts to 13 to 16 per cent by volume, which is termed "asphaltum."

The sludge tar consists on an average of 65 per cent tar and 33.5 per cent free sulphuric acid. For purification it was mixed with cold water to remove nearly all free sulphuric acid. The remaining lumpy material was melted over hot water and then carbonate of soda added until it remained slightly alkaline. During this operation it was noticed that at the beginning SO_2 and H_2S were generated, so that it seems possible that also hyposulphates were present in the tar. The melted bitumen was finally washed with hot water until neutral, and then, after removing the

*From Oil, Paint and Drug Reporter; translated from the Chemiker Zeitung.

water, was finally dried at a temperature of 100 degrees Centigrade. After cooling it forms a solid material, which can scarcely be distinguished from the better grades of asphaltum.

For analysis the bitumen was placed in a retort and distilled with the aid of steam. The following was obtained:

	Per cent.
Oil, specific gravity 0.865 at 15 degrees C., boiling points 105-302 degrees C.	50
Hard bitumen, melting point 149 degrees C.	50

The obtained oil was of a light yellow color and had the odor of unsaturated hydrocarbons. It was cooled to 0 degree Centigrade, at which temperature a considerable amount of wax was separated. This wax was not paraffin wax mechanically thrown down during the acid treatment of the crude oil, but solid, unsaturated hydrocarbons of waxy nature and soluble in sulphuric acid, specific gravity 1.835.

The yield of wax from the above distillate was 3 per cent; the melting point of the product was 51 degrees Centigrade.

The remaining oil, free from wax, showed the following chemical behavior:

$KMnO_4$ in aqueous solution—reduced at once, proof of double bonds.
$AgNO_3$ is ammonical solution—reduced on standing.
$HgCl_2$ conc. solution—resinous precipitate on shaking with the oil.

The reaction with $HgCl_2$ was pursued further. A larger amount of the oil was shaken with corrosive sublimate and left standing for twelve hours. The resinous substance settled to the bottom of the vessel while the balance of the oil floated on the top of the solution. The rosin was separated from the oil and the aqueous solution. Obtained were five grammes of rosin from 100c and oil. The resinous compound, which is insoluble in petroleum naphtha, behaves like a gum rosin. It can be stretched into threads like gutta percha, is soluble in chloroform, benzol, carbon bisulphide, etc., and possesses an odor resembling the ichthyol hydrocarbons. Since nothing is separated from crude oil by $HgCl_2$, this rosin must have been formed by the acid treatment. As at present I have no combustion apparatus at hand, I have to postpone an elementary analysis of this very interesting compound.

The hard bitumen obtained in the foregoing analysis was analyzed and was found to be composed as follows:

	Per cent.
Bitumen	95.1
Sulphur	3.2
Ash	1.7

To obtain further information of the bitumen it was boiled three times with acetic anhydrid. After each boiling the hot solution was decanted and the different fractions were mixed. The yellow rosin which separated out on cooling was collected. The acetic anhydrid solution was mixed with an equal volume of water and left standing in the hot water bath. After six hours' standing the solution was neutralized with carbonate of soda. The precipitated yellow rosin was collected. The dark residue from the acetic anhydrid treatment was extracted with benzole, which yielded a beautifully iridescent dark rosin. The residue was incinerated. During this operation a decided odor of burned sugar was developed. The analyzed bitumen yielded the following:

	Per cent.
Light yellow rosin, soluble in hot acetic anhydrid	6.30
Yellow rosin, soluble in cold acetic anhydrid	63.00
Dark rosin, soluble in cold benzol	4.50
Not determined	26.20

The sludge tar obtained from the treatment of crude Oklahoma oil with sulphuric acid is, according to the above analyses, composed of unsaturated hydrocarbons in loose combination with H_2SO_4 rosin and wax, besides some sulphur, which is partly formed by the reduction of the H_2SO_4 by the hydrocarbons. Of interest is the formation of the artificial rosin from the tar distillate by corrosive sublimate. I intend to take up this subject at a later date.

In addition to the article by Ed. Donath, "The Coals and Their Residues by Carbonization" (*Chemiker Zeitung*, 1912, page 373), according to which certain coals when melted with caustic potash yield dark solutions which give characteristic precipitates on acidification, I beg to state that I carried out similar reactions with asphaltum several years ago.

When melting asphalt from Beaumont or Oklahoma crude oil with caustic soda a dark aqueous solution is obtained which, when treated with an excess of chlorine gas, gives a pure white precipitate. This precipitate when filtered off, washed and dried, yields a yellow rosin. This behavior of asphaltum seems to indicate that petroleum, and especially asphaltum, are partly of a vegetable origin. As is well known, lignite is soluble in hypochlorites and asphaltum shows a similar behavior, as is shown above.

An interesting feature connected with the mining of bituminous coal in the United States in 1912 was the continued increase in the production by the use of machines, both in actual tonnage and in the proportion that the machine-mined output bore to the total. The total production of bituminous coal in the United States increased from 405,907,059 short tons in 1911 to 450,104,982 tons in 1912. The quantity of coal undercut or otherwise mined by the use of machines increased from 178,158,236 tons in 1911 to 210,538,822 tons in 1912. The increase in the total production was 44,197,923 tons, or 10.9 per cent, and the increase in the output by the use of machines was 32,380,586 tons, or 18 per cent, the increase in the production of machine-mined coal being equal to 75 per cent of the total increase in the production of bituminous coal in 1912 over 1911. The percentage of machine-mined coal to the total output has increased each year since the first successful undercutting machines were installed.

NEW SODA PROCESS FOR WOOD.

A patent has been granted to Josef Eduard Pfiel, of Vienna, assignor to the firm of Fr. Julius Schreyer, of Bremen, relating to a process for the manufacture of cellulose from wood, wood chips, straw, reed, and like materials. The following description of the process is taken from *Paper:*

The invention, says the inventor, relates to a process of manufacturing cellulose from fibrous material. In known processes of this kind it was only possible to use pieces of wood having a uniform degree of hardness and being freed of knots and bark as raw material. In all of these methods the lye, in which the material was boiled, acted upon the material until all of the largest part of the incrusting substances was dissolved therein. This necessitated the use of a large amount of lye and other chemicals and required considerable time. The particles near the surface of the layer, upon which the lye acted, usually were overboiled, that is, the fiber was destroyed or damaged, while particles near the center were not sufficiently changed to free the fiber from the incrusting substances. It was therefore necessary to maintain the lye in circulation through the material and to continue the boiling for a relatively long time.

The new process therefore consists in its preferred form essentially of three steps, namely, a swelling up of the incrusting substances, a mechanical opening of the fiber by a removal of the swelled up incrusting substances, and finally, if necessary, a de-gumming for the removal of the last traces of incrusting substances.

In the present process finely divided fibrous material spread out in a relatively thin layer of about 12 to 20 inches thickness is boiled in lye for a time only, which is sufficient to swell the incrusting substances, so that the same loosen their hold on the fiber which they surround. The boiling temperature may rise to about 200 degrees Centigrade under a pressure of about 220 pounds per square inch. As a suitable boiling liquid I prefer to use pure caustic soda lye of low concentration, for instance 2 to 4 per cent. The time for which the boiling is continued depends upon the material to be used and upon the lye, as well as upon the consistency to which the material is to be converted.

The incrusting substances partly separated from their fibers, and having then a jellylike structure, are removed from the fibers by washing. For this purpose the material is subdivided and strong jets of water are passed therethrough, which carry the jellylike substances along while the fiber is precipitated.

For the purpose of removing the last traces of incrusting substances the mass is degummed by adding thereto solutions of permanganates of potassium or other permanganates in suitable dilution. This has an oxidizing effect upon the residue of incrusting substances, which are converted thereby into a granular condition, and which may be dissolved by adding sulphurous acid.

The boiling of the raw material in lye may take place in relatively small vessels of tubular shape, having a diameter of 12 to 20 inches, and being several yards long. As only comparatively small quantities of raw material are subjected to lye at a time, it is obvious that the action thereof will be uniform throughout the material. The tubular vessels may be heated by gas, for instance, gas produced from chips, lye residue or by steam or by both. If they are heated by steam care must be taken that the condensate of the steam should not lower the degree of concentration of the lye; it is, therefore, of advantage to have a lye of somewhat stronger concentration at the beginning of the process, or introduce superheated steam to decrease condensation.

The heating temperature may be regulated to suit requirements. It is advisable to have a high temperature and pressure at the beginning for a short time, say for half an hour and to continue the boiling at a moderate heat, for instance for an hour, so as to lower the pressure. The heat may be entirely shut off when the charge is removed from the boiler.

It is also possible to remove the charge from the boiler after the first short heating operation, and to store it in tanks, which contain the lye. The partial separation of the incrusting substances may be continued without any external heat.

The washing operation, following the boiling, may be performed by passing the material through hollanders, commonly used in the manufacture of paper and such like. In a device preferably used for this purpose strong jets of washing liquid are conveyed through the material which is disposed on sieves. The jets wash the incrusting substances and short fibers through the perforations, while the long and good fibers remain on the sieve and form a felt-like structure.

In known methods of manufacture of cellulose the lye diffused partly into the fiber, so that it was necessary to bleach the same. The bleaching medium had to react upon the fiber; in the present process, however, the fiber is obtained in white and lustrous condition and no bleaching is required. In former methods the bleaching was effected by oxidizing the material by means of potassium permanganate, while in this process the permanganate acts upon the incrusting substances only and the sulphurous acid dissolves the same.

Under a new process which the Standard Oil Co. of Indiana is installing, at Whiting, it is believed that it will be possible to convert 75 per cent of crude petroleum into gasoline. The process opens the way for breaking up the hydrocarbons of petroleum into the combinations needed and condensing them under compression.

THE LABORATORY

METHODS OF ANALYSIS USED IN THE LABORATORIES OF THE ARMOUR INSTITUTE OF TECHNOLOGY.

The Analysis of Silicates.

The methods for the analysis of silicious materials, whether natural or artificial, are described and discussed at length by William F. Hillebrand in Bulletin No. 305 of the United States Geological Survey. These stand as the world's standard methods, and any radically different methods are almost out of the question. Hillebrand, however, gives a number of different procedures for some of the determinations, and the standpoint of his work is that of the most accurate scientific analysis, made under ideal conditions of equipment, and without the necessity of speed.

The methods here described are in the main, the methods of Hillebrand. Where there is a choice of procedure, those given are in the judgment of the writer, the most practical and rapid. Where modifications or changes are made, the object of the change is to make the determination more rapid or more simple, or to obviate the necessity of elaborate special apparatus which is frequently unavailable in a laboratory for the general practise of chemistry. In the methods here described the highest scientific accuracy is not sought. They are believed, however, to be of a degree of accuracy sufficiently high to answer any purpose other than the most exact requirements of mineralogical or geological research. Only the equipment of a good general analytical laboratory is required.

The materials which may be analyzed by the following methods include all silicious rocks such as quartz or sand, feldspars, shales, cement rocks, clays (both natural and artificial, including fire clays and all silicious refractories), silicious limestones, and indeed any oxidized silicious material which is not completely decomposable by acids.

The Sample.—It is assumed that the material for analysis is correctly sampled and that the sample has been crushed or ground. Any ordinary method of grinding will be insufficient for the analysis, so a few grams of the sample is ground by hand with agate mortar and pestle until it is so fine as to feel barely gritty between the teeth. It should all be able to pass fine bolting cloth. The so-called "diamond mortar" is recommended for the crushing preliminary to the final grinding in agate. When the ordinary steel disc pulverizer or bucking board is used it is inevitable that some extraneous iron get into the sample. According to Lenher* this may amount to more than 2.0 per cent with very hard materials such as quartzite, and to less but still appreciable amounts with softer substances. Before grinding one should decide whether or not this amount of iron will change the significance of the analysis. Ordinarily it will not.

THE ANALYSIS.

The following substances are always determined: SiO_2, total Fe (calculated to Fe_2O_3), Al_2O_3, CaO, MgO, K_2O, Na_2O. Besides these constituents some, if not all of the following are frequently determined: TiO_2, FeO and Fe_2O_3, MnO, Cr_2O_3, SO_3, P_2O_5, CO_2, H_2O. Of coures no analysis is truly a complete one unless all of the substances mentioned above have been determined or proved absent, together with several possible ones not mentioned. The commercial analysis of a silicious material is usually called "complete" when the first list of constituents has been determined and the sum of the percentages is nearly equal to 100. In such a "complete" analysis the sum cannot possibly be very close to 100 per cent without the effect of balancing errors, as will be pointed out hereafter.

The analysis for the constituents given in the first list will be described first.

The analysis is carried out upon two samples (or two sets of duplicate samples), the one for the main analysis and the other for the determination of the oxides of the alkalis sodium and potassium.

The Main Analysis.—The one-gram sample is weighed into a platinum crucible of about 20 to 25 grams weight. Upon this is placed about 4 gms. of the purest sodium carbonate and the material and flux mixed with a stout platinum wire or a small glass rod, care being taken to avoid loss. The crucible is now covered and heated, at first gently, and finally at the full heat, over a bunsen burner for about fifteen minutes when it is placed over the blast for five minutes or over the Meker burner for ten. This should give complete decomposition of any sample. When fusion is complete, the crucible is seized with the tongs, and, after cooling to a dull red heat in the air plunged for half its depth into cold water. This will make the melt easily removable, all but a little of it coming out in a single lump when the crucible is gently tapped over a casserole. This lump in the casserole is covered with water (about 25 cc.) and warmed. Meanwhile the small residue left in the crucible is treated with water and dilute HCl directly in the crucible, and all the material dissolved and

*Jour. Ind. Eng. Chem., Vol. 4, p. 47.

transferred to the casserole, the latter being covered to prevent loss through the effervescence of the CO_2.

Any particles that stick to the walls of the crucible or to the inside of the cover are easily removable by the aid of a glass rod together with the water and acid. Now to the main mass in the casserole is added conc. HCl until there is no further action, the lump being broken up from time to time to prevent the insulation of undecomposed material by the precipitated silicic acid. This will usually take about ten cc. of acid. After all effervescence ends and the lump is completely disintegrated the cover-glass is rinsed off, the whole boiled for a few minutes and finally evaporated to dryness on the water bath or on a thick asbestos board heated by a bunsen burner, all boiling being avoided. The dry residue is now thoroughly drenched with conc. HCl and after a few minutes boiling water forced in from the wash bottle, about 50 to 75 cc. being used. The whole is then boiled for a few minutes and after settling, filtered and the residue which contains over 95 per cent of the SiO_2 washed with hot water containing a little HCl about three times. The filtrate is re-evaporated, and after complete drying is heated for an hour or more at a temperature of 110° to 120° C. This residue is saturated with strong HCl, taken up in water, boiled, and the silica filterd off upon the paper containing the main bulk of the silica from the first separation of that substance. The whole is washed with water containing a little hydrochloric acid, and finally with hot water. This precipitate contains all the silica originally present in the material, except an insignificant amount which remains in the filtrate. If the filtrate were again evaporated and the process for silica repeated, about a milligram more of silica might be recovered. This amount is not important, however, and as it will distribute itself among several determinants made upon the filtrate, it occasions no serious error later on in the analysis.

The residue is then ignited wet in a weighed platinum crucible, and finally blasted for about five minutes, when it is cooled in a dessicator and weighed. The weight is total silica (except the trace mentioned above) together with a ponderable quantity of the oxides of iron and aluminum and a part of any TiO_2 and P_2O_5 that the sample might have contained. To correct for the weight of these oxides, the SiO_2 is completely expelled by adding to the moistened contents of the crucible about 5 cc. of HF solution and a drop of conc. H_2SO_4, and evaporating the whole to dryness on the hot plate. The residue of oxides is blasted for two or three minutes and finally weighed. The difference in weight between the first weight of the crucible and total contents and the weight of the crucible and the small residue of oxides, is the weight of silica. This is ordinarily taken as the total SiO_2, and this weight when divided by the weight of the sample and multiplied by 100 is the percentage. The residue after the volatilization of the silica is usually very small. It contains besides small amounts of ferric oxide and alumina, a part of the titanium as TiO_2 and of the phosphorus as P_2O_5. When more than three or four milligrams of oxides remain, considerable amounts of the latter substances are suspected. The weight of this residue is determined by subtracting the weight of the empty crucible. The crucible is not cleaned at this point, but is kept with the residue in it for the ignition and weighing of the precipitate of ferric oxide and alumina (etc.) which is obtained next. In this way the correction for the amount of these oxides retained by the silica is applied directly.

Determination of Ferric Oxide and Alumina (etc.) —The filtrate from the determination of the silica contains the great bulk of the basic material of the sample in the form of chlorides, together with most of the SO_3, P_2O_5 and TiO_2. This solution, in a Jena or other resistive-glass beaker, is made distinctly alkaline with 1:1 ammonia solution and acid again with hydrochloric acid of similar strength. The solution is now raised to boiling and 1 gm. of pure ammonium persulphate added. Ammonia solution is added slowly until present in fair excess as indicated by the odor, and after boiling a few minutes the precipitate is filtered, and washed three times. The precipitate is dissolved in hot dilute HCl containing a little sulphurous acid, from a wash bottle, the paper washed clean and the precipitation repeated exactly as before. (It is well to pour a little dilute ammonia over the filter after washing). The ammonia used should be free from carbonate, so that no calcium be precipitated. For greatest accuracy it is well to redistill it. At least it should come from a fairly fresh bottle. The ammonia and hydrochloric used as above has assured enough ammonium chloride to prevent the precipitation of magnesia, except in dolomitic limestones. In that case more ammonium chloride should be added. The precipitate and paper are placed in the crucible containing the residue of oxides after the volatilization of silica, and heated gently until the paper is completely consumed, after which the heat is raised, and the ignition finished by a ten-minute heating over the blast.

The ignited precipitate which is weighed at this point contains, besides the ferric oxide and the alumina, Mn_3O_4, TiO_2 and P_2O_5.

Treatment of the Precipitate of Fe_2O_3, Al_2O_3 Mn_3O_4, P_2O_5, TiO_2.—In this precipitate iron is determined volumetrically, and in case P_2O_5 and TiO_2 are later determined upon separate samples of the rock, the weight of Al_2O_3 is obtained by subtracting the weights of each of the other constituents from the total weight of the precipitate. This gives the most satisfactory determination of alumina. In case the P_2O_5 and TiO_2 are not determined, the difference between the weight of the whole precipitate and the weight of the ferric oxide is called the weight of the alumina. This will always be high, but frequently will answer the purpose.

The iron in this precipitate is determined as fol-

lows: To it, in the crucible, is added about two grams of potassium pyrosulphate. ($K_2S_2O_7$ is prepared by gently igniting $KHSO_4$ until frothing due to the elimination of water ceases). The whole is then fused, a bright red heat being finally attained. The fusion, while still liquid, is poured into a cold, dry platinum dish, and after cooling, is dissolved in hot water containing sulphuric acid, the part of the fusion remaining in the crucible being rinsed out with hot dilute H_2SO_4 and added. The solution contains all of the iron as ferric sulphate. Any small residue remaining undissolved is silica that was not removed at first. It is generally insignificant in amount. If, however, it is desired to determine it, the solution is evaporated until copious fumes of sulphuric acid are evolved, cooled, taken up in water, and filtered. The residue after washing, is ignited and weighed as silica and its percentage of the whole sample added to the original per cent of silica. The iron in the solution is now to be reduced and titrated with permanganate solution by one of the following methods:

(a) The solution is thoroughly saturated with hydrogen sulphide gas. This reduces the iron from the ferric to the ferrous condition with precipitation of sulphur, and also removes any traces of platinum that have gotten into the solution. (There will always be some platinum from bisulphate fusion). This solution is boiled to coagulate the sulphur and filtered into a 500 cc. flask, stoppered with a doubly perforated stopper, and hydrogen sulphide run in through a tub for a few minutes. The hydrogen sulphide generator is replaced by a generator (such as the Kipp) supplying a rapid stream of carbon dioxide. This gas is passed into the solution, which should be kept gently boiling until all hydrogen sulphide is removed, as shown by test of the escaping gas with paper saturated with lead acetate. Failure to give a black color on the paper shows the complete elimination of the hydrogen sulphide. At this point, the solution is allowed to cool with the current of carbon dioxide still flowing, and when cold, it is titrated with permanganate solution to the first permanent pink. The permanganate solution should be much less strong than the ordinary laboratory solution, which is usually of about tenth-normal strength. A proper solution is prepared by taking 100 cc. of the ordinary standard solution and diluting it to exactly 500 cc. in a measured flask, care being taken that solution and water be at the right temperature. This solution is about N/50, and its iron standard is exactly 1/5 that of the original solution.

$$\frac{\text{No. of cc. of } KMNO_4 \times \text{standard}}{\text{Weight of sample}} \times 100 = \% \text{ Fe}$$

$\%$ Fe $\times$ 1.4294 $=$ $\%$ Fe_2O_3.

$\%$ mixed oxides $-$ $\%$ Fe_2O_3 $=$ $\%$ Al_2O_3 (approximate).

(b) The iron in the solution may be much more rapidly and simply, although less accurately determined as follows: To the sulphate solution in a 250 cc. Erlenmeyer flask is added about one gram of granulated zinc (about 20 mesh is best) together with a pinch of sodium carbonate to form CO_2 and help drive out the air. A small funnel is placed in the mouth of the flask and the solution warmed gently until all of the zinc has gone into solution. The colorless solution is then cooled rapidly under the cold-water tap and titrated at once with the permanganate, as described above. If the zinc is not known to be free from iron as determined by a blank experiment conducted exactly as above, a weighed amount of zinc must be used and the correction made upon the total volume of permanganate solution used by subtracting the volume known to have been used by the iron in the zinc. The great defect of this method lies in the fact that titanium if present in the original substance would be present at this point, and the titanic sulphate would be reduced by zinc and oxidized again by the permanganate, thus giving a false (high) result for iron. On the other hand, the titanic sulphate is not reduced by hydrogen sulphides, and so would not effect the result for iron. If titanium is absent or present in minute quantity, the second method for iron is fairly satisfactory, and is recommended for ordinary work on account of its simplicity.

(To be continued.)

In addition to the administration of its waste lands for forest purposes, the individual state should play a part in cooperating with private timberland owners, commensurate with the interest which the state has in maintaining its timber supply. This principle is enunciated by the committee on state forestry at the national conservation congress. The committee further recommends as general principles for the practice of state forestry everywhere that the governing board should be removed from partisan political control, and that the state forester should be fitted for his work by professional training and experience. Civil service should govern in the selection of all forest officers, and all industries directly dependent on the forests should be represented on the state forestry board. Further, the committee says, the forest officers should have ample discretionary power, and should be delegated enough authority to settle controversies as they arise. After an organization is formed it should be provided with machinery which will make its work effective, such as ample funds, a sufficient force, prompt and effective measures against forest vandalism, and a strong police power. Without including all these things, the committee says, state legislation will fail of its purpose and largely be a dead letter.

The nitrate production of Chile for the year ending June 30, 1913, amounted to 59,450,454 Chilean quintals (quintal = 101.41 lbs.), against 54,572,965 quintals for 1912, with consumption for the same period at 54,908,912 quintals against 52,985,430 quintals for 1912.

METALLURGY

USE AND DEVELOPMENT OF REFRACTORIES IN THE IRON AND STEEL INDUSTRY.*

By HARRY W. CROFT.†

The requirements in the iron and steel industry, for refractories, are itemized briefly thus:

Blast Furnace.—For a blast lining three kinds of brick are made: For the hearth and bosh a brick of maximum refractoriness and one capable of resisting the action of the fused or semi-fused furnace contents; for the inwall a brick to stand high heats and abrasion; and for the top a dense and tough brick to withstand the wear of the stock and resist the action of the gases.

The introduction of the water cooled furnace, with its lining of 12 in. or less, necessitated the use of the highest grade of refractories available. This was accomplished by a mixture of clays giving the minimum of shrinkage and by manipulation designed to increase their bond to the maximum. The brick were finally made into 12-in. blocks on a steam press.

Several years ago a committee appointed by one of our largest iron and steel interests made an exhaustive study of refractories to combine practical operating experience with the knowledge of the brick maker in producing, if possible, better brick. The result of their study of blast furnace linings led to a specification for blast furnace brick calling for a minimum of impurities and of consequently higher refractoriness than the standard linings. Two hand-made linings were made under this specification. A few years previous, at the request and with the co-operation of a well-known blast furnace manager in the Chicago district, several linings were made, with the object of producing a lining somewhat more refractory and at the same time denser and tougher than the standard linings. These were hand made, also.

In summarizing the three developments cited it is of interest that each of the three efforts to improve the old standard lining approached the problem from a somewhat different angle:

The making of the steam pressed linings for the thin lined furnace aimed directly at a brick of much greater density and toughness, without sacrificing any refractoriness.

The second method undertook to materially increase the refractoriness of the brick, at the same time maintaining, if possible, the bond of the standard furnace brick.

The object of the third method was to increase both the refractoriness and toughness of the brick, in a lesser degree, possibly, than in the other two cases, but without materially increasing the cost.

At present blast furnace men are calling for the hand-made and machine-made linings in about equal numbers. The present machine-made lining includes as many as possible of the good points of the first steam-pressed lining referred to, without all of the extra treatment of clays and consequent higher cost. In one point apparently the machine-made brick should be superior, and that is in furnace tops. It is also possible to make it of more regular and uniform dimensions than by the hand-made process, thus insuring better brick laying.

Hot Blast Stoves.—In hot blast stoves fire brick act merely as a thermal reservoir, yet are subject to widely varying temperatures, to enormous loads, and in many cases to the fluxing action of the flue dust in unwashed gases.

Piping and Connections.—Although in blast furnace and stove piping and connections high temperatures are not involved, mere density in the brick is insufficient; toughness is requisite. In recent years a high-grade brick specially designed for this use has proved economical.

Open Hearth and Soaking Pit.—What we have said of stove brick applies to the checker brick used in open hearth furnaces and soaking pits. Here again the tendency is unquestionably toward the use of a higher grade brick.

Heating Furnaces.—The practice in many heating and welding furnaces is particularly severe on brick, for we encounter here extremely high heats and often sudden variations in temperature. Limited as we are by the refractoriness of the clays at our disposal, any substantial betterment in results must come from improved furnace design, or the substitution of silica for clay brick.

Boiler Settings.—A remarkable development in the use of fire brick for boiler settings has taken place in recent years. It was but a few years ago that the words "boiler brick" were synonymous with a second or third grade material. To-day no fire clay brick is considered too good if it materially lengthens the service. For the side walls many are finding a blast furnace brick economical, and even expensive bauxite brick is sometimes used because of its greater resistance to clinkering. Under modern conditions of increased grate areas, mechanical stokers and forced draft, any or all of which may be involved in the common practice of working boilers from 50 per cent to

*From a paper presented before American Iron and Steel Institute at the Chicago meeting, Oct. 24.

†President, Harbison-Walker Refractories Co., Pittsburgh.

150 per cent over rated capacity, the problem of the boiler setting is no small one.

Gas Producer.—At first sight the gas producer has no real lining problem, yet to-day certain producer manufacturers have entirely discontinued the use of other than the highest grade of brick, and are experimenting with various linings, including bauxite brick.

SILICA BRICK.

We believe the silica brick of to-day are better than they were several years ago. The workmanship is better; the brick are tougher. In the open hearth, whether basic or acid, its use is no longer restricted to the side walls, blocks and roof, but is extending to the checkers, roofs and walls of the regenerators. But a few years ago an average of 250 or 275 heats was considered fairly good. To-day an average of 400 to 500 heats is not uncommon, and single runs up to 800 or 900 heats are frequent.

By-Product Coke Oven.—In the by-product coke oven is seen the greatest development of recent years in the use of silica brick, displacing clay and quartzite brick completely above the oven floor and in certain portions beneath. This use of silica brick is wholly an American development. A few years ago 24-hour coke was normal; to-day by the use of silica, with its greater refractoriness and conductivity, it is possible to make 15-hour coke.

Crucible Practice.—In Eastern crucible practice silica has to-day displaced clay brick in fully 90 per cent of the tonnage.

Heating Furnaces.—We have in heating furnaces one of the newer uses. It has in gas fired pipe welding furnaces proved a great economy and is adopted wherever there are no sudden changes of temperature. In the roof of large span and small rise the absence of shrinkage gives silica an advantage.

Boilers.—As a whole, there are in the boiler arch too rapidly varying temperatures to render its use satisfactory, but where the boilers are gas fired, and sufficient care is exercised to prevent sudden changes of temperature, the worth of silica brick has been demonstrated.

BASIC, OR MAGNESITE AND CHROME.

The introduction of the open hearth process for making steel called for a refractory material for lining the bottoms and sides of furnaces that would resist the action of basic slag. The major portion of magnesite and magnesite brick used in the iron and steel industry is for the bottoms of basic open hearth furnaces and in the side walls extending above the slag line. This material is also widely used in the ports and blocks, and many furnaces are now being constructed where the end walls and uptakes are built of it. The bottoms and side walls of electric furnaces of certain types are also of magnesite. Magnesite brick are being generally adopted in iron and steel furnaces wherever basic slag is encountered.

CHROME ORE.

Chrome ore, or chromite, is coming into general use in steel making on account of its refractoriness and resistance to both acid and basic slags. In the form of brick this material is used in open hearth furnaces, soaking pits and dolomite kilns. It is also ground and used as a patching and daubing mixture for repairing jambs, side walls, ports and blocks of open hearth furnaces.

CONCLUSIONS.

In summarizing this review of the use and development of refractories there are certain points that will bear emphasis, even at the expense of repetition:

We note the frequent use of magnesia and chrome brick to resist basic slags, displacing a high grade of fire clay brick.

We see silica brick displacing clay brick where the maximum refractoriness is required and where the variations in temperatures permit.

We have a higher grade of fire clay brick displacing the lower.

In these, as well as other instances that might be cited, this tendency is apparent, namely, the gradual substitution of the higher grade refractories for the lower.

The number and variety of difficult shapes is fast increasing. Brick work is laid with greater accuracy. To-day less than half the clay or cement formerly used for laying is employed.

As in other lines of manufacture, specifications are becoming more rigid. Fire brick manufacturers are now working under specifications that several years ago were considered impossible.

The brick maker is somewhat limited in his efforts to develop his product by the fact that in the past 25 years no new beds of fire clay of a quality better than formerly used have been discovered. These clays all have their well-defined limits of refractoriness. He is therefore to meet new conditions confined to a mixture of known clays in various proportions, with suitable additions of calcined clay; to grinds of various degrees of fineness; to burns of varying degrees of hardness; and to special treatment of the clays. After a careful hand selection, any effort to increase the refractoriness by a further elimination of even a small percentage of impurities involves much rehandling in their weathering and washing, which is costly.

The future development of refractories will be interesting. The uses of silica are fast increasing; the field for basic refractories is widening, and it is probable that further refinement in the making of fire brick will justify the cost. This development presents problems for the iron and steel manufacturer, as well as the brick maker, and we venture the opinion that with their continued co-operation much can yet be accomplished toward meeting the constant demands of the iron and steel industry in their efforts to increase their output.

THE NOMENCLATURE OF NON-FERROUS ALLOYS.*

Dr. G. K. BURGESS.†

We are witnessing an unprecedented activity in the development of the non-ferrous industries accompanied by the search, often rewarded with brilliant success, for new combinations of metals suitable for special uses. It is only very recently, however, comparatively speaking, that the equilibrium diagrams of our most common alloys such as the simple brasses and bronzes have been established, and most, if not practically all, of the three-component systems to say nothing of the more complex ones, are still to be determined.

The art of preparing, mixing and applying them to industry in many cases has preceded by centuries the science of the constitution of the commoner non-ferrous alloys, and some of them possess names that date from times immemorial which no one would think of endeavoring to change—nor is this necessary.

The question arises, however—it has arisen before and been put aside as inopportune or hopeless of solution—whether it is not worth while, in view of the rapid development of special alloys to which are assigned a bewildering chaos of meaningless names, to endeavor to make provision for a more orderly naming of the non-ferrous alloys.

NUMERICAL DESIGNATIONS.

Imagine what would be the status of the nomenclature of organic chemistry to-day if there had not been developed at an early date a rational system of naming in terms of the constituents based in part on the existing names of the more common organic compounds, and I think we should all agree that the complexity of organic chemistry is at least as great as that of the non-ferrous alloys.

In the realm of ferrous alloys and their naming, although there is some confusion, it is not nearly so bad as with the non-ferrous alloys. Some rational-minded person, or persons, started saying ferro-silicon, ferro-manganese, etc., and the force of a good example soon established the habit of this simple nomenclature which is being rationally extended by the more precise numerical defining of terms such as 40 ferro-silicon, 60 ferro-silicon, etc., to indicate the percentage of silicon or other element in the ferrous alloy. Such a numerical method has been tried in a few instances also for some of the non-ferrous alloys, for instance to indicate the nickel content in German silvers, but this practice is by no means generally in vogue in either realm.

AVOIDING PERSONAL, OR "COINED," NAMES.

We may cite another example—this time to avoid—from ferrous nomenclature, namely, the microscopic constituents, which, following the barbarous practice of the mineralogists, have been named after distinguished metallographists and metallurgists. These names were becoming of embarrassing number and beginning to create confusion as to their meaning and distinction, when the International Society of Testing Materials, at its Copenhagen meeting, endeavored to eliminate this confusion by reducing the number of terms used and defining them exactly. Fortunately, this phase of needless confusion and antiquated method of nomenclature of microscopic constituents has not yet arisen in the case of any of the non-ferrous alloys, and there is no reason why the mistake of such bad practice should be made a second time, since there are adequate names in the ordinary language of physical chemistry to provide for naming rationally all such constituents.

Personal and "coined" names have been used, however, quite extensively in naming particular non-ferrous alloys or classes of alloys having very distinctive properties. The extent to which this practice should be encouraged in the future is a debatable question, but, anticipating the future in terms of the past, in those cases for which an alloy or group having sharply characteristic properties is discovered, particularly if it be of a very definite or of a somewhat complicated composition, there may be no great disadvantage, perhaps, in not entirely discouraging this practice of naming. Its great disadvantage over a rational system of naming is the tax on the memory as the number of such alloys multiply, and I believe that in general the practice of applying personal or "coined" names should be discouraged. Deliberately misnamnig an alloy to give it a more valuable-sounding name, or for other purposes, it seems to me, should be emphatically frowned upon by such a society as this. Such monstrosities as "manganese bronze"—to mention but one flagrant case—do not reflect credit on any technical body of men accepting them.

HARMONIZING THEORY AND PRACTICE.

It is necessary, or, at least, highly desirable, if an effort is to be made to rationalize the naming of non-ferrous alloys, that there be co-operations on the part of several classes of persons, ranging on the one hand from the practical foundryman or manufacturer to the scientific man, as represented by the physical chemist and metallographist, on the other hand, in order that a system of naming may be devised which will harmonize theory and present practice and provide adequately for the future.

No foundryman need fear that his empirical and convenient practice of numbering serially or otherwise labeling the alloys he makes will be interfered with, as he is evidently free to adopt any system he pleases within his works. Nevertheless, a common system of naming, or identification and classification, becomes imperative where several manufacturers are in competition; and it is furthermore evident that in drawing up or meeting specifications, a common language is equally desirable. Clear-cut definitions of alloys will serve oftentimes as a protection to the seller, and will aid the intelligent buyer. There is a gradual tendency towards uniformity in naming as the literature

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†U. S. Bureau of Standards; Chairman Committee on Nomenclature of Institute of Metals.

of the subject grows and becomes crystallized and new books on alloys appear, but this effect of written precedent permeates but slowly.

FIXING SPECIFIC LIMITS.

It is also evident that in framing a system of nomenclature, it would be advantageous to consider the desirability of fixing practical tolerance at least for some of the more common alloys and perhaps the principles on which such tolerances—or variations in the product from an accepted definition—can be worked out without too great difficulty. It is here that a knowledge of the equilibrium diagrams will be of the greatest importance, since for some alloys the division line between two adjacent phases having very different properties is very sharp, while for others there is a gradual transition in properties, with change in composition. It is evident that specifications for the composition of the latter type may be less rigid than for the former in the region of a dividing line between two phases. In a more refined non-ferrous metallurgical age, we shall undoubtedly see the manufacturing conditions and thermal treatment also specified with precision.

A derived question, but one that it might be well to consider in this connection, is the extent to which impurities or cheaper components in excess shall be allowed in certain alloys and within what limits such alloys shall retain the simpler name to which they might otherwise be entitled.

CO-OPERATION OF TECHNICAL SOCIETIES.

It is evident without further instances that the subject is a very broad one, requiring a great deal of painstaking study and skillful handling, but I believe it is a subject demanding urgent attention. In fact, I do not need to remind you that the British Institute of Metals, at the suggestion of Mr. Rosenhain of the National Physical Laboratory, has taken up the question in co-operation with a committee from several of the British technical and scientific societies.

I believe that the subject is of such great importance and has so many aspects—even including geographical—that I would advocate this society taking the initiative in America in the formation of a joint committee on non-ferrous nomenclature, comprising representatives from the interested societies in America, such as the American Institute of Metals, the A. S. T. M., the American Chemical Society, the American Institute of Mining Engineers and, eventually, the International Society of Testing Materials, as well as the British societies.

The estimated value of the gold produced in the Alaska portion of the Yukon basin in 1912 was $8,645,000, compared with $9,050,000 in 1911. This decrease is due to the falling off of the output from the Fairbanks and Hot Springs districts, for the other Yukon camps either held their own or somewhat increased their output compared with the preceding year.

HISTORY AND PROBLEMS OF THE STEEL WHEEL.*

By D. F. CRAWFORD.†

The development of the wrought steel wheel has been of interest to the management of the railways from two viewpoints, namely:

(1) Its use as a substitue for the steel tired built-up wheel of various patterns used for passenger equipment cars and locomotive tenders. (2) Their application to freight carrying cars, especially those designed for mineral traffic, instead of the cast iron wheel generally used.

Even in the early stages of the development it was apparent that the wrought steel wheels could be produced at prices which would warrant their introduction in lieu of the steel tired wheel, and consequently a considerable number of them are now in service under passenger cars and the heavier locomotive tenders.

The results obtained with the wrought steel wheels in such service indicate equal safety, with decreased investment and maintenance cost, as compared with those formerly used.

While wrought steel wheels are now used in large numbers for freight carrying cars, the length of time in such service has not been sufficient to give really conclusive information as to the relative economy of the wrought steel and cast iron wheels, especially the cast iron wheels of the recently strengthened designs, and made under improved methods of manufacture.

The data available, however, indicates that in the wrought steel wheel at present prices the cast iron wheel has at least found a competitor, and that a further reduction in the price of the steel wheel will probably lead to their more extended use for freight car purposes.

Quite a number of freight cars of 100,000 pounds capacity, built immediately after their advent in 1898, were provided with cast iron wheels of the lighter designs and as practically all cars of the capacity named, built in the earlier years, were for mineral traffic, the combination of light wheels and heavy work resulted in more frequent failure and rapid wear than was desirable. Notwithstanding the fact that the weight of the cast iron wheel has been increased from time to time, it cannot be said that cast iron wheels in general use to-day give as good results for cars of 100,000 pounds capacity as was obtained with similar wheels for cars of 60,000 pounds capacity.

The above mentioned conditions, coupled with the construction of cars having capacities as high as 140,000 pounds, carried on eight wheels, without doubt extended the use of the steel wheel and stimulated their production.

As an indication of what service may be expected

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*From the discussion before American Iron and Steel Institute, Chicago, Oct. 24, 1913.

†General Superintendent of Motive Power, Pennsylvania Lines West, Pittsburgh.

from the steel wheel, the fact that records of the mileage of a number of wheels under 100,000 pounds capacity cars in freight service, show that an average of about 180,000 miles per wheel has been obtained without reaching a condition requiring turning. This mileage represents from 18 to 22 years of service under the average freight car.

Accurate information regarding the mileage of cast iron wheels under cars of 100,000 pounds capacity is, unfortunately, not available, but from records made in 1907 it was found that the average age of the number of wheels removed from service, from cars of 100,000 pounds capacity, was 4 years, corresponding to a mileage of from 32,000 to 40,000 per wheel.

As there can be no question as to the relative strength of an equal section of wrought steel and cast iron, it would seem that for cars of 100,000 pounds capacity and over, the steel wheel must have preference from this viewpoint.

The Pennsylvania Railroad System has followed with interest the development of the wrought steel wheel practically from its inception, and has made use of them in considerable numbers during the entire period of its development, and at the present time they are used exclusively for—

Locomotive Tenders—Passenger Service.

Locomotive Tenders—Freight Service (over 5,000 gallons capacity).

Passenger Equipment Cars (where the weight per wheel exceeds 10,000 pounds).

Freight Equipment Cars (gondola and hopper cars of 100,000 pounds capacity and greater, for mineral and mill traffic).

The lighter tenders, passenger cars and freight cars of less than 100,000 pounds capacity, as well as the box, refrigerator and stock cars of 100,000 pounds capacity, are provided with the cast iron wheels.

Up to the present time about 325,000 wrought steel wheels have been purchased and the results obtained indicate the desirability of continuing the practice referred to.

Of the total number of 325,000 wrought steel wheels purchased, but 328, or about one-tenth of one per cent, have been withdrawn from service on account of breakage or cracks.

Of these defects 164 were located in the tread, 69 in the plate, 50 in the plate and hub, and but 45 in the flange.

The small number of defects located in the flange is particularly interesting, as it is at this point that the cast iron wheel of the design in general use has the least strength.

The majority of the 329 wheels referred to were used under heavy locomotive tenders, and is, therefore, representative of the effect of the hardest kind of service.

As these defects are those which occurred during the entire period of development of the steel wheel, and the number includes many manufactured under the less perfected processes at first employed, it is to be expected that even a more favorable record will be obtained in the future. In fact the processes now in use should practically eliminate the tread defects, as the larger portion of such defects were undoubtedly due to the effects of "pipes" in the original ingots.

The defects in the plate, and plate and hub are probably due to shrinkage strains, and their number clearly shows the desirability of further study as to the cause and means for their elimination.

Quite a large number of the wheels as at first manufactured gave short service life on account of lamination of the treads (the same defect was frequently found in steel tires of the smaller diameters), but with the wheels as now made, the number having laminated treads is comparatively small.

On the application of steel wheels to mineral carrying cars it is the practice of the Pennsylvania System to increase the nominal carrying capacity from 100,000 pounds to 110,000 pounds; thus increasing the permissible loading from 110,000 pounds to 121,000 pounds.

As there is no doubt of the wheel having ample strength to permit obtaining the full capacity of the axles, this increase in capacity not only adds to the earnings obtained with the vehicle, but assists in keeping them always provided with a full set of steel wheels, as this kind of wheel only is the standard for cars of over 100,000 pounds marked capacity.

The construction of many freight carrying cars of over 100,000 pounds capacity still further broadens the field for the use of the steel wheel, and makes necessary the further strengthening of the cast iron wheels on the lines already indicated by the manufacturers.

The South African Mining Journal notes in a recent issue a change in metallurgical practice on the Rand. In the past all the mills installed on Witwatersrand mines were 22 ft. long by 5 ft. 6 ins. in diameter—dimensions that for some years have been regarded as "standard." Lately, however, the new Van Ryn Deep (80-stamp installation) and the Consolidated Langlaagte (100-stamp plant) put in 16 ft. 6 ins. by 6 ft. tube mills. The South African Mining Journal continues: "For some time there has been a feeling among Transvaal metallurgists generally that mills of less length than the "standard" 22 ft. by 5 ft. 6 ins. would do more economical work, and exhaustive experiments were carried out at a leading Witwatersrand mine with a view to determining the most efficient size of tube mill. These researches have gone a good way toward proving that mills of even smaller dimensions than 16 ft. 6 ins. by 6 ft. will more nearly approach the ideal as regards the combined considerations of capacity, efficiency, and cost. It is expected that these tests, when concluded, will have an important and far-reaching effect on Rand ore-reduction methods, and that in the future such new mills as may be installed on the Witwatersrand will be of substantially less length than the "standard" 22 ft.

FUEL POSSIBILITIES IN STEEL MAKING.*

By WILLIAM WHIGHAM.†

The limits of the paper are, briefly, the fuels used in steel making proper and the possibilities of American practice. In the manufacture of steel no single item is of greater importance than that of fuel. The high temperatures at which the metals separate from the elements with which we find them associated in nature and at various stages of manufacture have placed our fuels on a plane of equal importance with the raw materials themselves, and their location has firmly intrenched certain districts as strongholds of iron and steel production. The natural fuels which enter into the making of steel proper are found in the solid, liquid and gaseous states. The liquid and gaseous forms generally belong to that numerous group of combinations of hydrogen and carbon designated as hydro-carbons. For the purposes of this discussion all fuels may primarily be divided into two groups.

GROUP I.

This group comprises those fuels which come to the steel maker as a component part of the metals with which he works, as, for instance, the carbon, silicon, manganese and sulphur contents of the pig iron. While not generally referred to as fuels in this connection, yet these are as truly fuels and perform much the same function as those which occur as such in nature and require more or less preparation for the purpose intended—that is to say, the maintenance of a temperature sufficiently high for the thermo-chemical reactions to take place.

The fuels listed under this class as occurring in the iron received by the steel maker require little attention, as their quantity and consumption, within certain limits, and the methods of their combustion are both approximately fixed.

They are of great importance in the Bessemer process, furnishing as they do the sole fuel used in this branch of steel making. One gross ton of representative Bessemer iron contains about the following:

Element.	Per Cent.	Pounds.	Heat Value—Per Lb. B. T. U.	When burned to	Total heat value in gross ton of Bessemer metal B. T. U.
Iron	93.67	2,098.2	.....	....	.....
Sil'n	1.45	32.48	12,600	SiO_2	409,248
Car.	4.00	89.6	14,500	CO_2	1,299,200
Mng.	.75	16.80	2,975	MnO	49,980
Sul.	.04	.90	.....	....	.....
Phos.	.69	2.62	.....	....	.....
Total	100.00	2,240.00			1,758,428

As the sulphur and phosphorus are not oxidized to any extent in the Bessemer process, no heat value has been assigned them. Practically all the silicon, carbon and manganese are burned in the process, and it will be seen from the above table that the heat equivalent for oxidation of the entire quantity of these three constituents amounts to only about 1,750,000 B. T. U. per gross ton of iron blown, or, say, 2,000,000 B. T. U. per ton of steel ingots produced. This is equivalent to 148 pounds of coal having a heat value of 13,500 B. T. U. per pound. It will be seen from this how efficient the Bessemer process is as regards fuel consumption when compared with the Open Hearth process using 450 to 600 pounds of fuel per ton of steel in addition to the fuel content of the iron itself.

Were no metallurgical question involved, the Bessemer process of making steel would probably never have been replaced.

The matter of phosphorus elimination, however, has compelled recourse to the Open Hearth process where low phosphorus steel is a consideration.

GROUP II.

This group comprises those fuels which are found in nature as such and must be adapted through more or less preparation and through the use of extraneous equipment to the purposes of the steel maker. In what is perhaps the order of their importance they are as follows:

Bituminous Coal.—Under this heading are also included the products of coal, namely, tar and by-product coke-oven gas.

On account of its wide occurrence, proximity to the other raw materials entering into the making of steel, low cost and ease of conversion into a gaseous state, bituminous coal will probably always be the most generally used fuel in the making of steel by the open hearth process. It is found in great quantities in Western Pennsylvania, West Virginia and Southeastern Ohio, which renders it available for use with local fluxes, Lake and imported ores; in Alabama and Tennessee in close proximity to ore and limestone beds there; in Indiana and Illinois near the Lake ore supply; and in Colorado and Wyoming close to the western ore supplies. It will be thus seen that, both from the standpoint of quantity and location, bituminous coal has a position in the manufacture of steel not easily replaceable by any other fuel.

The proximate analyses and heat values of the coals of the four above-mentioned districts are about as follows:

Group—	Per Cent Fixed Carbon.	Per Cent Volatile.	Per Cent Moisture.	Per Cent Ash.	B. T. U. Per Lb.
A	50-60	30-40	1-1½	6-10	13700-14200
B	70-75	15-20	½- 1	5- 7	14500-15000
C	45-50	30-35	1- 5	10-12	12000-13000
D	40-50	30-40	5- 8	10-12	11000-12000
E	35-40	35-40	2- 4	20-25	10000-10300
F	40-45	35-40	13-17	4- 8	10300-10700

Key: Group A, Penna., W. Va., and Ohio (high volatile); B, Penna., W. Va., and Ohio (low volatile); C, Alabama and Tennessee; D, Indiana and Illinois; E, Wyoming and Colorado (bituminous); F, Wyoming and Colorado (lignite).

*From a paper presented before American Iron and Steel Institute, at the Chicago meeting, Oct. 24, 1913.

†Assistant to the President, Carnegie Steel Co., Pittsburgh.

Utilization.—The coals utilized in steel making by the open hearth process are used in the following ways:

Through Gas-Producers.—On account of its simplicity of operation, the gas producer has to the present time been the means most generally employed for the utilization of coal in the making of steel in the open hearth furnace. Steel works engineers are not unanimous as to the advantages of one or the other of the two classes of gas producers (hand stoked and mechanical); this is probably due in this instance, as in many others connected with engineering and industrial operations, to a lack of accurate data concerning the performances of the two classes of apparatus. Generally speaking, the choice ought to be made on the following points: cost of installation, cost of operation, labor supply, efficiency.

The first cost, based on large installations, will be about the same per open hearth furnace served, and may be stated in round numbers as $2,000 per furnace in either case, which figure includes four hand-poked or two mechanical producers with all coal and ash handling equipment complete. The rated capacity of a 10-foot hand-poked poodncer is 1,000 pounds of coal per hour gasified; the average actual capacity is about 800 pounds per hour, and as a rule about four of these producers are installed for each open hearth furnace. The rated capacity of the mechanical producer is about 2,000 pounds of coal per hour and its actual operating capacity in the neighborhood of 1,600 pounds per hour. Up to the present time it has been usual to install two mechanical producers per open hearth furnace; but in some cases five producers have been installed for two furnaces, and it has been suggested that the larger furnaces, making 90 tons of steel at a heat, have three producers each. It can hardly be said that this large producer capacity has been yet justified by results.

A comparison of the cost per ton of coal gasified, including maintenance and repairs as well as direct labor and supplies, for two large plants, shows the following:

Cost to gasify a gross ton of coal (2,240 lbs.) hand-poked equipment	$0.745
Cost to gasify a gross ton of coal (2,240 lbs.) mechanical equipment	.444
Difference in favor of mechanical installation	$0.301

This difference is practically all in the direct labor, as will be seen from the figures below, taken from the same cost sheets:

Direct labor cost to gasify a gross ton of coal, hand-poked equipment	$0.509
Direct labor cost to gasify a gross ton of coal, mechanical equipment	.213
Difference in favor of mechanical equipment	$0.296

These figures indicate about two and one-half times as much labor for the hand-poked as for the mechanical installation, and the whole disadvantage of this excess labor is not indicated by the extra cost. The difficulty at times in securing labor for this purpose is an important element in the decision.

Both types of producer will deliver to the furnace, either in form of sensible heat or heat of combustion, 85 to 90 per cent of the total heat in the coal received by them. Average combined producer and furnace practice will show about 550 pounds of coal to the ton of steel, or 7,425,000 B. T. U., based on 13,500 B. T. U. per pound of fuel.

The conclusion of the writer from the above data is that the mechanical producer should be used in all large installations. It would appear also, from the fact that the mechanical producer has been perfected to an extent where it requires less than one-half the labor for the older type, and, as stated above, shows from 85 to 90 per cent efficiency as a gas-making apparatus, that radical improvements in its operation are hardly to be looked for. The principal losses, being loss of fuel in the ash and radiation from the producer itself and piping carrying the gases to the furnace, can hardly be expected to be reduced any considerable amount.

As By-Products of Coal viz.: Tar and Coke-Oven Gas.—The by-products of coal, such as tar and coke-oven gas, present greater opportunities for advancement in fuel efficiency, but have their limitations on account of quantity available.

Wherever tar can be obtained in sufficient quantities, its use has been attended with considerable success. Practice in burning tar as a fuel for steel-making purposes shows that from 30 to 35 gallons of tar to the ton of steel is easily attainable, and as each gallon contains on an average about 160,000 B. T. U., the total heat in the fuel required to make a ton of steel tar is about 5,200,000 B. T. U. as compared with 7,425,000 B. T. U. in the case of average producer practice, or about 70 per cent. This is partially accounted for by the fact that the radiation and other producer losses in the case of coal are not present where tar is used. The figures given above, namely, 30 to 35 gallons of tar per ton of steel, were obtained on a 40-ton furnace and represent by no means the economy which might be looked for on a larger furnace. The method of burning tar is to heat it by steam coils to a point where it will readily flow and inject it in an atomized condition through the bulkhead wall of the furnace. Many types of burners have been tried, but nothing better has been found than the simple device consisting of a tar tube inside a tube through which the atomizing air is blown, both tubes being drawn to a relatively small orifice at their delivery ends. The pressure of air used for atomizing is about 80 pounds.

The cost of installation, including tar tanks, pumps, air compressors, etc., is small, being in the neighborhood of $1,500 to $2,000 per furnace. As to the possibilities of tar as a fuel for steel making, its limitations are, as stated above, in quantity rather than in any other direction. The uniformity and degree of heat attainable are all that could be expected by the steel maker, but, in view of its comparatively limited

production and used in many other directions, it is hardly likely that it will attain any great prominence as a steel-making fuel.

Experiments with by-product coke-oven gas for steel making have been few, and practically no data is available. The quantity of this gas is rather too small in amount and can be utilized so easily to advantage in other directions that it is hardly likely that it will be much of a factor in steel making. It has been used to a considerable extent in the heating of steel for rolling mill purposes and seems to be perfectly satisfactory for this use.

Pulverized Coal Burned Directly.—One of the most promising methods of using coal, both as to the low first cost of equipment and economy in fuel consumption expected from the process, is in the pulverized condition. Coal in this condition has been for some time used in the burning of cement, in puddling furnaces, in steel-heating furnaces and to some extent under steam boilers. Its advent as a steel-making fuel has taken place only very recently. The principal points to be taken care of, as seen at the present time, are, a thorough drying of the coal, pulverizing to a degree of fineness which will permit 90 per cent of the fuel to pass through a 200-mesh sieve, and its injection into the furnace in a uniform stream. The high flame temperatures possible with pulverized coal properly burned has suggested that the regenerators in the open hearth furnace might be replaced entirely with waste heat boilers, which are of course a much more efficient means of reclaiming waste heat than fire-brick used as regenerators. In any event, the use of coal in this way, which injects its entire ash content into the open hearth furnace, and a large part of it into the passages and checkers beyond the furnace, is going to require a modified design of regenerator. On account of the recent adoption of pulverized coal in steel making, this detail has not been thoroughly worked out.

Natural Gas.—This fuel for the making of steel, as indeed for all other purposes for which fuel is used, is ideal. The only place where it is found in sufficient quantities to be available for steel making is in western Pennsylvania and West Virginia fields. Its average composition and heat value are about as follows:

Carbon Monoxide (CO)	1.493
Methane (CH_4)	93.96
Ethylene (C_2H_4)	1.447
Nitrogen (N_2)	3.10
	100.00

B. T. U. per cubic foot.....1,048.

On account of its small volume and weight per unit of heat it is not necessary to regenerate it, nor is it possible to do so on account of its composition, as it breaks down at comparatively low temperatures.

The method of burning in the open hearth furnace is simply to carry the gas pipe through the bulkhead of the furnace and bring the gas into intimate contact with the regenerated air. Temperatures are thus attained fully ample for the requirements of steel making. The lack of the necessity for regenerating the fuel gas leaves the entire regenerator space available for preheating the air.

The quantity of natural gas necessary for the production of a ton of steel ingots by the open hearth process is about 5,500 cubic feet, having a heat value of 5,766,750 B. T. U. It may vary somewhat below or above this figure, depending upon the size and construction of the furnace and the care with which it is used by those in charge. In the making of steel, and in fact in most metallurgical processes, there is much room for economy, the necessity for which becomes more apparent as the permanency of the supply is threatened. Reliable figures covering the actual heat loss, etc., in an open hearth furnace using natural gas are available. In the summary which it is intended to make of the question of furnace efficiencies the results obtained from a furnace working on natural gas will be used. As is the case with tar and by-product coke-oven gas, the limitations as to the use of natural gas in steel making are also found in the supply. In the Pittsburgh District, where natural gas has been used most for the making of steel, it is hardly likely that new open hearth furnaces will be constructed without some kind of coal-burning equipment; and even in the other requirements of steel making, such as ingot heating and reheating, it will also be found desirable to follow along these lines. Probably within a period of 5 to 10 years, unless unanticipated discoveries are made of natural gas supplies in the way of larger and more numerous wells, this fuel will be confined to domestic purposes and the smaller manufacturing operations.

Crude Mineral Oil.—Reference to this fuel is mainly historical as applied to the making of steel as, on account of the present high cost, it is hardly available for this purpose. It was never used in very considerable quantities, and those works which have used it have been compelled to adopt other fuels. The method of burning it was to atomize it in a burner let through the bulkhead of the furnace in much the same manner as coal tar is used. The consumption was about 45 to 50 gallons, or 5,826,600 to 6,474,000 B. T. U., per ton of steel.

POSSIBILITIES OF HIGHER EFFICIENCIES IN OPEN HEARTH CONSTRUCTION.

Up to this point nothing has been said about the possibilities of better furnace design in order that fuels may be used more efficiently in the furnace. Realizing the lack of specific information in this respect, a thorough test has been carried out on a 50-ton furnace using natural gas, the test having been made on a furnace using this fuel on account of the ease with which the fuel could be measured and the avoidance of inaccuracy through having to take into consideration fuel losses external to the furnace, as is the case in the use of producer gas.

Beginning with Sept. 27, 1911, accurate measurements were taken of the quantities and temperatures

entering into the making of 469 heats, occupying a total of 233 days, 2.78 hours. The results averaged for the 469 heats show that 12.95 per cent of the total heat available was found in the steel at tapping time; 1.79 per cent was in the tapping slag; 1.23 per cent in the pit slag; 1.57 per cent and .97 per cent were used in reducing the ore and decomposing the limestone, respectively; 30 per cent was absorbed and returned to the furnace by the regenerators; 30.02 per cent was carried up the stack, leaving 19.47 per cent for radiation, conduction and unaccounted for. The thermal efficiency of the furnace and regenerators combined, based on the ratio of the first six items enumerated above to the total heat supplied, is shown to be 48.5 per cent. The thermal efficiency of the regenerators is shown to be 38.3 per cent measured by the ratio of the heat delivered to the incoming air to the total heat in the waste gases leaving the bridge wall.

An examination of these figures indicates that there are two items which can be controlled by design and operation. They are:

Radiation and Conduction Losses. — These vary greatly with the construction of the furnace. Thicker walls will prevent the escape of the heat of the furnace, but at the same time will probably result in higher cost of upkeep due to more rapid deterioration while the walls are still thick. The choice between this and the greater fuel loss, due to thinner walls, involves a considerable amount of judgment. It is impossible to determine without much experiment just where the economical point lies; but it would appear from the construction of a great many open hearth furnaces that a large amount of heat might be saved by thicker and better walls, particularly around the bulkheads and ends of the furnace.

Stack Losses.—The following shows the average analyses by volume of the stack gases from 469 heats:

Constituents.	Per Cent.
CO_2	5.31
O_2	13.05
CO	00.00
N_2	81.64
	100.00

A study of this analysis will show that there is about two and one half times as much air present in the stack as is needed theoretically for combustion of the gas. This large excess of air reduces the flame temperature, and the water carried into the furnace as moisture in the air also has a material effect on the temperature. The average flame temperature with the 150 per cent excess air was 3,074 degrees. By approaching the theoretical amount of air required higher temperatures might be obtained, thereby reducing the volume of waste gases and the time required per heat, and so lead to fuel economy. To reduce stack losses the temperature and weight per hour of the waste gases must be reduced, and to do this it is absolutely essential to have control of the air supply. This control cannot be had by throttling the air at the remotest source of supply, namely, the air inlet valves, as the furnace is not air-tight and supplies its demand through the slag hole, around the door frames and other openings, this leakage not only entering without preheating but coming in where least needed for combustion. Theoretically, one cubic foot of gas requires 9.2 cubic feet of air for complete combustion. The air meters measured in this experiment on an average 13 cubic feet of air through the checkers for every foot of gas consumed and the leakage through the furnace was 10 cubic feet or 77 per cent excess above that measured.

Effect of Reversal Intervals.—In the heating and cooling effects of the waste gases and air as measured at the furnace or "hot" end of the regenerator chamber and at the stack or "cool" end of the regenerator chamber, we find that, for 20-minute reversals, the gas at the hot end of the regenerator works between 1,675 degrees, Fahrenheit, at the beginning of the heating period and 2,125 degrees, Fahrenheit, after the gases have been passing through the regenerators for 20 minutes, while at the cold end of the regenerator chamber the gases have a temperature of 645 degrees, Fahrenheit, at the beginning of the heating period and rise to 1,415 degrees at the end of the 20-minute period. The point of greatest significance is that, after the gases have passed for 10 minutes, further absorption by the checkers is only obtained at the expense of comparatively high stack temperatures, the conclusion in general being that reversals should be of as short an interval as possible consistent with the maintenance of temperatures sufficient for the purposes of the furnace. As a matter of fact reversals on this particular furnace have been cut down to 15 minutes, with an increase in fuel economy and reduced repairs on the furnace. The temperatures not working over so great a range lead to less wear and tear on the brickwork of the furnace.

Waste Heat Boilers.—One other method of recovering the heat in the stack gases offers itself to the engineer, and that is the use of waste heat boilers beyond the checkers, and this method is being used with a high degree of success. One of its disadvantages is the large capacity of boilers required for a given recovery on account of the comparatively low temperatures of the gases. A 75-ton open hearth furnace must be fitted with a 400 horsepower boiler in order that 200 to 250 horsepower of steam may be developed. Notwithstanding this and other disadvantages, an installation of open hearth waste heat boilers will give a good return on the investment, particularly in localities where fuel prices are high.

Duplex Process.—Recent developments in the "Duplex" process have shown a reported fuel consumption of 150 to 180 pounds of coal per ton of steel, which might be expected from the high thermal efficiency of the Bessemer part of the process, and it is highly probable that, if these results are borne out by continued practice, the most economical consumption in steel making will be obtained by the use of this

process, in which the open hearth portion will be carried on with the most economical method of burning fuels as outlined above, namely, some form of fuel consumption in which the entire combustion takes place within the furnace walls, supplemented by furnace construction which will permit of a minimum radiation, large checker chambers with comparatively frequent reversals, and waste-heat boilers between the checker-chambers and the stack.

A brief summary of all the fuel possibilities for steel making is as follows, the fuels being listed in the order which they have been treated above.

SUMMARY.

Fuel Contents of the Metals.—Developments in the Duplex process may give an increased importance to this item.

Bituminous Coal.—Any considerable advancement in fuel utilization will probably be found in improvements in the methods of applying this fuel to the uses of the steel maker. These will likely be confined to the use of coal in the solid state, as its by-products are too limited in quantity to become an important factor in steel making and producer practice cannot be expected to advance radically, but the burning of coal in a pulverized condition presents possibilities.

Natural Gas.—Limitations are found in quantity.

Crude Oil.—Because of the limited production and high cost, this will likely become a factor of diminishing value.

The U. S. Consul at Leeds, England, reports that at the Selby mills of Moss, Rimmington & Co. (Ltd.) tests have been made with flax straw from Montana that seem to have resulted very successfully. Many attempts have been made to treat the American fiber, but so far either the cost of treatment has been too great or the methods suggested have proved commercially impracticable. What appears to be a practical, commercial, and inexpensive solution of this problem has been worked out by Mr. George Pearson, formerly of Nottingham, England, but now of Great Falls, Mont., in conjunction with the Messrs. Foster of Selby. The flax straw can be taken direct from the field, treated very rapidly, dried by the sun, passed through special machinery, and put upon the market at a minimum of cost and time. The fiber retains the full original strength, twine spun from it withstanding a higher test than twine of the same size made of Russian Siretz hemp. Messrs. Pearson and Foster say they are convinced, after many experiments, that their treatment can be applied with commercial success to flax straw grown in any part of the United States, and that the resultant fiber can be made into all varieties of yarn and twine, including binder, packing, and shop twines.

Copper exports for the week ending Oct. 30, last, totaled 3,616 tons. Since Oct. 1 they were 27,689 tons.

GERMAN TESTS OF BENZOL AS A MOTOR FUEL.

During the early part of the summer a 9-day test of light gasoline, heavy gasoline, and benzol as fuels for pleasure and other light motor vehicles was conducted under the direction of the Imperial Automobile Club and the Association of German Automobile Manufacturers. The cars entered were divided into three groups. On the first day group 1 was provided with light gasoline, group 2 with heavy gasoline, and group 3 with benzol. On the second day the cars of the first group were provided with heavy gasoline, those of group 2 with benzol, and those of group 3 with light gasoline, and so on. The following particulars of the test are given by Consul General A. M. Thackara of Berlin, in the Daily Consular and Trade Report:

Prior to each run, the committee in charge reports, exact tests were made of the fuel to be actually used. The heat units per kilo (2.2 pounds) found to be contained in each fuel and the tested specific gravity of each at 59° F. were as follows:

Fuel.	Heat units per kilo.	Specific gravity.
Light gasoline	10,402	0.715
Heavy gasoline	10,282	.757
Benzol	9,576	.879

The prices of the three fuels to retailers f. o. b. nearest railway station at the time of the trials were as follows per 100 kilos (220.46 pounds): Light gasoline, $12.08; heavy gasoline, $7.85; benzol, $7.38. One hundred kilos of gasoline of a specific gravity of 0.75 equal 35 gallons in volume; 100 kilos of a specific gravity of 0.88 equal 30 gallons.

The cars that took part in the trials were of 8 and 10 horsepower. The horsepower referred to is taxable horsepower, the legal formula for calculating which is $PS = 0.3 \times I \times D \times S$, in which PS stands for horsepower, I for the number of cylinders, D for the diameter of the cylinders, and S for the length of the stroke in meters.

The approximate average rates of speed maintained during the trials by the two classes of cars were:

Fuel.	Miles per hour— 8-horse-power.	10-horse-power.
Light gasoline	26.2	28.4
Heavy gasoline	26.3	28.6
Benzol	26.5	28.4

The total car mileage recorded with each fuel, each being used three of the nine days, was: Light gasoline, 1,596.3 car miles; heavy gasoline, 1,615.6 car miles; and benzol, 1,770.3 car miles. Calculated on the basis of the volumetric consumption of light gasoline during 1,596.3 car miles, the corrected car mileage for each fuel, assuming that a like volume of each was used, is: Light gasoline, 1,569.3 car miles; heavy gasoline, 1,629.9 car miles; and benzol, 1,851.7 car miles.

On the basis of these results and the prices given above it is calculated that the fuel cost per unit of distance was 32 per cent lower with heavy gasoline

than with light gasoline for the 10-horsepower cars and 33 per cent lower for the 8-horsepower cars. With benzol the saving as compared with light gasoline was 35.75 per cent for the 10-horsepower cars and 32.6 per cent for the 8-horsepower cars. The committee makes the following comment:

How far automobile users may realize the foregoing results, favorable as they are to heavy gasoline and benzol, depends on the development of fuel production and the future organization of the fuel market, and also on the solution of the difficulties attending the carburization of the heavy fuels in low temperatures.

The reference to conditions of fuel production and marketing has to do with the fact that the output of benzol in Germany is controlled by an association of coke manufacturers. As to the difficulty of carburizing benzol and heavy gasoline in low temperatures, the committee comments as follows:

Unfortunately, as a result of the warm weather which prevailed during the trials, the disadvantage of the heavy fuels, namely, the difficulty of carburization in low temperatures, did not appear, and more definite information on this point must await further trials. Difficulties of carburization can be overcome by a preliminary warming of the air, by the admixture of fuel of less specific gravity, such as gasoline, or by alteration of the chemical make-up of the fuel, but in all cases with a partial loss of economy.

On the question of carburetors the committee makes the following statement:

This special, technically interesting point was established by the trials, namely, that it is quite possible with one and the same carburetor and without special adjustment to vaporize all three fuels, though differing from each other considerably in their specific gravities and chemical composition, and still obtain thoroughly regular operation. That economy of fuel naturally results from careful adjustment of the carburetor, and was as a matter of fact attained in an increasing degree in the course of the trials, goes without saying, and is a fact which may not be lost sight of in the regular use of either of the heavier fuels. But that special carburetors are necessary for the proper use of heavy gasoline and benzol, as was often said and accepted prior to these trials, has been shown to be an error, which can best be disproved by the fact that not one of the manufacturers participating in the trials used a special carburetor. On the other hand, carburetors were exclusively employed such as are used in the equipment of the regular output of the factories in question with the one difference that a suitable warmer was provided.

Many cold-storage plants are being erected in different parts of Russia. A well-known bakery in Moscow is constructing its own storage plant, and cold-storage houses are to be constructed in the Okhotnyi Riad, the chief food market of Moscow. The erection of cold-storage plants is also being planned in many provincial towns, such as Nizhni Novgorod, Vladikavkaz, Kharkof, and Archangel. A joint-stock company recently organized in St. Petersburg has purchased a large area of land in the Siennaya Ploshad district of that city and proposes to erect a building housing stores, banks, etc., including a large cold-storage plant. The work is under the direction of the engineer who constructed the extensive cold-storage plant of the Petersburg Store Co. (Ltd.)

COMMERCIAL YIELD OF OIL IN COPRA.

The Manila Merchants' Association having noted a Hamburg report in *Daily Consular and Trade Reports* for March 5, 1913, in which it was stated that the yield of oil in copra was 63 per cent, asks whether this yield is realized in the experience of German manufacturers, or whether the figures stated represent the total oil content of the raw material. The matter has been carefully investigated, and there seems to be no doubt that the average commercial yield of oil in copra is 63 per cent in the experience of German crushers. This yield leaves a cake with a content of 6½ to 7 per cent of oil, and at times the cake contains even as much as 11 per cent.

Fresh cocoanut kernels contain from 30 to 40 per cent of fat, sun-dried copra contains as much as 50 per cent and kiln-dried copra considerably more—sometimes as much as 74 per cent. It is inevitable, of course, that any process that practically eliminates the content of water in the raw material raises proportionately the content of fat in the resultant product. Lewkowitsch states that the mean content of fat in copra obtained from 21 analyses was 68.3 per cent. In these tests the maximum percentage was attained in copra from the Pacific Islands and was 74.72 per cent. Malabar and Ceylon copra came next with 71 per cent, while Manila copra yielded in some instances 67 and 68 per cent, and had a low record of 64.7 per cent.

The above figures from Lewkowitsch refer to total oil content. The Hamburg crushers expect to obtain an average of 63 per cent of oil, as first stated. In a single pressing of the raw material the variations are said by a well-known machinery manufacturer to be from 60 to 66 per cent. Both hydraulic and continuous-process presses are in use in Hamburg and both types of presses are manufactured in this country. The continuous-process press is of American invention, and it is understood that the license to build it in Germany is held by the Krupp-Gruson Werke in Magdeburg. According to information at hand, both types of presses have their special advantages, the continuous-process press being particularly useful in dealing with soft kernels, while the hydraulic presses are more particularly available when the material at hand is hard and tough.

The production of potato flour in Holland increases rapidly from year to year and the product is also steadily finding markets abroad. The total production is now not less than 275,000,000 pounds annually. The price rules lower now than it did a year or two ago. Much of this flour is finding a market in the United States, where it is used for starch manufacture. The following statistics of the amount declared at this consulate in the past years is indicative of the growing export business in potato flour from Holland: 1910, $38,000; 1911, $58,287; 1912, $290,025; 1913 (8 months), $121,486.

FRENCH ALCOHOL PRODUCTION AND USES.

Consul General Frank H. Mason, Paris, reports that the French Ministry of Finance has just published some very interesting statistics concerning the production and use of alcohol in France. The total production in 1912 was 87,440,420 United States gals., as compared with 63,797,165 gals. in 1911. In spite of this enormous production, France received from foreign countries 4,913,571 gals. of pure alcohol and liquors. On the other hand there was a total export trade of 8,321,370 gals.

For the first time details are given of the use made of alcohol produced. In all, 40,044,517 gals. took the form of beverages, a small quantity was used for the manufacture of perfumery, and 17,994,896 gals. were denatured. About 2,306,130 gals. were employed for mixing with wine, to increase its alcoholic degree of strength, and thus allow of transportation over long distances as in the case of export to foreign countries, and 1,490,106 gals. were used in the manufacture of vinegar. Out of the quantity taxed for consumption, 21,905,701 gals. took the form of "eau de vie," or brandy, 5,776,457 gals. were used for absinthe, and 282,557 gals. were used for making perfumery. The remainder was employed in the manufacture of different liquors. Of the 17,994,896 gals. of denatured alcohol 12,662,483 gals. were used for heating and lighting, while 4,113,504 gals. were employed for the manufacture of explosives.

The consumption of alcohol was lowest in the department of the Vendée, 0.919 quart per head of its population. The department of the Seine, in which Paris is situated, consumed 4.829 quarts per head, while the Calvados required 11.9299 quarts, and the Seine Inferieure 13.1970 quarts of alcohol per head of their respective populations.

In a recent paper presented by the American Institute of Metals, Dr. E. Weintraub, describes a method of making copper castings which are mechanically sound and of high electrical conductivity. This, heretofore, has been difficult of accomplishment on account of a porous character of copper castings. The improvement consists in adding boron, which, having a high affinity for oxygen, nitrogen and oxygen containing gases, is a natural deoxidizer for copper. One per cent of boron suboxide flux (equivalent to 0.08 to 0.1 per cent of boron suboxide) is added to the copper and a commercially sound casting is obtained. Any material containing boron in a state of oxidation below that of boric anhydride may be used as a flux for copper castings. In the foundry of the General Electric Co., Lynn, Mass., the boron flux is used in the following way. One-half of the flux to be added is mixed with charcoal, and is placed on the bottom of the pot, thus melting down with the copper. When the copper has reached the necessary temperature, the pot is taken out, the slag skimmed, and the second one-half of the boron flux is added and thoroughly stirred. The slag promptly comes to the surface in the form of fused lumps and is skimmed off, and the melt is cooled by the addition of gates or risers. If a reverberatory furnace is used for melting, the flux is usually placed in a ladle pot on the bottom, and the copper poured over it, and thoroughly stirred. Skimmer and stirrer should not be of iron, otherwise there will be a solution of iron in the copper, which will reduce the electrical conductivity. Graphite stirrers have been used successfully. The electrical conductivity can be as high as 97 per cent of the Matthiessen standard, and the mechanical properties of boronized copper are as follows: Tensile strength, 24,350 lb. per sq. in.; elastic limit, 11,450 lb. per sq. in.; elongation 48.5 per cent; reduction in area, 74.49 per cent.

WORLD'S PRODUCTION OF RAW SILK.

(Manchester Guardian.)

The following estimate of the 1913 world raw-silk production is taken from the Manchester (England) Guardian. While subject to revision, it may be taken as approximate. The table also gives the corresponding figures for 1912 for comparison:

Countries.	Production 1912. Pounds.	Production 1913. Pounds.
Western Europe:		
France	1,102,310	771,620
Italy	9,038,955	7,495,715
Austria-Hungary	661,385	705,480
Spain	176,370	176,370
Total	10,979,020	9,149,185
Far East (exports):		
China—		
Shanghai[1]	10,727,690	9,700,340
Canton[1]	4,797,260	5,291,095
Japan	23,849,600	24,471,310
India	396,835	330,695
Total	39,771,385	39,793,440
Levant and Central Asia:		
Servia, Bulgaria, Roumania	330,695	220,465
European Turkey	573,200	440,925
Greece and Crete	110,230	110,230
Brusa	925,940	1,212,545
Syria, Cyprus, etc.	1,146,405	1,433,005
Caucasus	881,850	661,385
Persia and Turkestan (exports)	1,102,310	1,212,545
Total	5,070,630	5,291,100
Grand total	55,821,035	54,233,725

[1]Excluding tussali.

According to the *Iron Age* a paint that is applied to the surface and then baked, and which is said to be a new rust-proof coating has the following composition: Linseed oil, 25 parts; calcium resinate, 36 parts; manganese-borate, ½ part; lead acetate, 1 part; naphtha 12½ parts; artificial graphite, 25 parts. The article is baked at 300° F. for one hour and 40 minutes, and the coating is stated to be highly lustrous and resistant to corrosion.

PRODUCTION OF PLATINUM.

Platinum is now worth $46 an ounce, against $20 five years ago. Increased prospecting last year in the United States, however, resulted in a total output of only 721 ounces of crude metal. The world's output is estimated by the Geological Survey in troy ounces as follows:

Country.	1910.	1911.	1912.
Russia	275,000	300,000	300,000
Canada	30	30	30
New South Wales	332	470	500
Colombia	10,000	12,000	12,000
United States, domestic crude	390	628	721
United States, from foreign and domestic matte and bullion	1,000	1,200	1,300
Borneo and Sumatra and other	209	.....	200
Total	286,961	314,328	314,751

Imports of platinum into the United States in 1912 aggregated $4,503,682 in value.

RECENT PATENTS.

The following patents relating to industrial and engineering chemistry are reported by C. L. Parker, solicitor of chemical patents, McGill building, Washington, D. C.

1,071,856. Treatment of *Metal-Bearing* Solutions. E. A. Ashcroft, Balestrand, Norway. Patented September 2, 1913.

1,071,873. Refining Process for *Iron and Steel* by Means of Ferrochromium Alloy. J. Buchel, Wengern-Ruhr, Germany. Patented September 2, 1913.

1,071,949. *Explosive.* J. F. O'Brien, Chicago, Ill. Patented September 2, 1913.

1,071,977. Method of Improving the Condition of *Flour.* J. A. Wesener, Chicago, Ill. Patented September 2, 1913.

1,072,032. *Explosive.* F. Raschig, Ludwigshafen-on-the-Rhine, Germany. Patented September 2, 1913.

1,072,034. Process for Bleaching Solid and Semi-solid *Fats* of All Kinds. F. Richter, Frankfort-on-the-Main and Ludwig von Orth, Berlin, Germany. September 2, 1913.

1,072,098. Gas-Producer. Emile Dor-Delattre, Liege, Belgium. Patented September 2, 1913.

1,072,373. Process of Producing *Cyanogen Compounds* and the Like. C. E. Acker, Ossining, New York. Patented September 2, 1913.

1,072,686. Process of Obtaining *Potash Salts* from Feldspar. H. P. Bassett, Baltimore, Md. Patented September 9, 1913.

1,072,904. *Rust-Proofing Iron,* Steel, or the Like. Augusto Bontempi, New York, N. Y. Patented September 9, 1913.

1,072,945. *Electrochemical* Process. Joseph L. R. Hayden, Schenectady, N. Y. Patented September 9, 1913.

1,073,116. *Caoutchouc* Substance and Process of Making Same. Carl Harries, Kiel, Germany. Patented September 16, 1913. The process comprises subjecting isoprene to the action of sodium.

1,073,129. Transparent *Waterproofing.* Aaron C. Horn, New York, N. Y. Patented September 16, 1913.

1,073,247. Process of Producing *Sulphate of Ammonia* from Ammoniacal Gases or Vapors. H. Koppers, Essen-on-the-Ruhr, Germany. September 16, 1913.

1,073,363. Deposition of *Metallic Salts* from Solutions Containing Them. H. J. Rees. Llansamlet, Glamorgan, Wales. Patented September 16, 1913.

1,073,523. Manufacture of *Sodium Alloys.* E. C. Rossiter, Birmingham, England. Patented September 16, 1913.

1,073,527. Substitute for *Rubber.* J. B. Scammell, London, England. Patented September 16, 1913.

1,073,587. Art of Making *Iron and Steel.* J. R. Billing, Birmingham, Alabama, September 23, 1913.

1,073,605. Method of Removing Impurities from *Coal-Gas.* G. H. Hultman, Stockholm, Sweden. Patented September 23, 1913.

1,073,845. Process of Producing *Caoutchouc-Like* Substances. Carl Coutelle, Elberfeld, Germany. Patented September 23, 1913.

1,073,932. Process for the Manufacture of *Fluorescent Substances.* G. Rupprecht, Hamburg, Germany, Patented September 23, 1913.

1,074,106. Process of Producing *Ozone* and Separating Gases. H. Dumars, Glen Ridge, N. J. Patented September 30, 1913. The process comprises reducing air to a temperature somewhat below the liquefying point for ozone, but above the liquefying point for oxygen and nitrogen, and at such temperature subjecting the oxygen of the air to the action of ozonizing means, and separately collecting the liquid ozone and the remaining gases of air.

According to statistics published in *Chemical News,* world's production of calcium carbide reached 300,000 tons in 1912. In Europe, Germany is the principal consumer of carbide. In 1911, 37,000 tons were imported, and in 1912 the importations amounted to 48,000 tons; no exportations were reported. Sweden produces the largest quantity of calcium carbide and consumers the least. The factories at Odda are capable of producing 80,000 tons per annum. In 1912 Switzerland exported calcium carbide valued at $1,000,000; Austria-Hungary exports about 11,000 tons per year; England imports only between 14,000 and 18,000 tons; while France imported 3,302 tons and exported 6,225 tons in 1912. It is especially the development of lighting by acetylene in the French colonies which has increased so regularly the exports of carbide.

The present coal production of China is estimated at 9,000,000 to 13,000,000 tons per year.

A U. S. Consular Report states that a Norwegian company has succeeded in producing 98 per cent nitric acid from the 30 per cent acid it has been producing at its Notodden and Rjukan plants for use in the manufacture of calcium nitrate.

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NOTES AND COMMENTS.

Natural Gas Consumption in Pennsylvania.

The natural gas industry of Pennsylvania surpassed in 1912 that of any previous year from almost every point of view. Except in 1908, which was a year of business depression, the quantity of gas consumed in Pennsylvania has continued to increase steadily, according to B. Hill, of the United States Geological Survey, until in 1912 the enormous total of 173,656,003,000 cubic feet was consumed. The gas was used largely for manufacturing and other industrial purposes, the quantity consumed for these purposes being 124,324,911,000 cubic feet, valued at $14,333,048, an average price of 11.53 cents a thousand cubic feet. The consumption of gas in this state in 1911 was 159,104,376,000 cubic feet, valued at $23,940,001, an average of 15.05 cents a thousand cubic feet. Pennsylvania leads all other states in the quantity of gas consumed.

In the industrial world the year 1912 was one of great prosperity, and natural gas is one of the fuels most needed and sought for. It is the ideal fuel for the manufacture of iron, steel and glass, for which the state of Pennsylvania is noted, and it is the presence of this gas in the fields of this state that has helped to make it the leading manufacturing state in the country. Since the introduction of natural gas into the industrial establishments of Pittsburgh in 1883, this district has continued to grow until it has become the greatest industrial center in the United States. It is estimated that more fuel is consumed in this city and its immediate vicinity and more coal and coke are shipped into and through the Pittsburgh district than in any other district of the world.

Borax Ore in California.

Deposits of colemanite, the calcium salt of boric acid, were discovered in Ventura county, California, in 1898, and the district has yielded about 35,000 tons of crude ore, valued at approximately $1,000,000. This colemanite, although classed among the few important deposits of this kind of ore in the country, has suffered the disadvantage of being a long distance from the main routes of transportation. As in the case of many other western industries, however, it is expected that the opening of the Panama Canal will greatly stimulate production. As examination of the borate deposits of Ventura county was recently made by Hoyt S. Gale, of the United States Geological Survey, and while the investigation was not sufficiently detailed to permit an expression of opinion as to the magnitude of the undeveloped deposits, it is believed that they are very considerable.

Fuller's Earth.

Bulletin No. 71 of the United States Bureau of Mines on the subject of "Fuller's Earth" has just been issued. Charles L. Parsons, the author, in the introduction says:

"The United States produces all of the Fuller's earth used for refining petroleum within its borders. On the other hand, most of the Fuller's earth used in bleaching edible oils has been imported from England. Recently a few of the refiners of cottonseed oil have begun to utilize domestic Fuller's earth, whereas others have been unable to substitute it successfully for English earth in their practice. Many samples of American earth distinctly superior in bleaching power to the English earth have come to the attention of the Bureau of Mines. For these reasons an investigation of the mining, preparation, and use of Fuller's earth in this country, especially in its application to edible oils, was conducted in order to ascertain why our own raw material has been deemed inapplicable to our needs.

"During the calendar year 1912, according to figures of the United States Geological Survey, there were imported into the United States 1,970 tons of unground Fuller's earth, valued at $11,619, and 17,139 tons of ground Fuller's earth, valued at $133,718, these values being based on the wholesale market price at the port of origin. The addition of transportation charges, commissions, etc., make the price to the American refiner $14.50 to $16 per ton. According to the latest figures compiled by the United

States Geological Survey, the United States in 1912 produced 32,715 tons of Fuller's earth, valued at $305,522 or $9.34 per ton, at the mine. Most of this domestic production was from three plants in Florida and one in southwestern Georgia and was used almost wholly for decolorizing petroleum. A small amount from other localities was used in the refining of edible oils. No figures definitely differentiating Fuller's earth from other clays are kept in regard to our exports, but it is certain that several thousand tons of domestic earth was exported to Germany, and it is also true that German refiners of edible oils have used and are using large quantities of American Fuller's earth and have a higher appreciation of its merits than our own refiners.

"As a result of the investigations made, the Bureau of Mines believes that the United States has Fuller's earth far better suited for refining edible oils than any imported, and that to assure the almost universal use of this earth by American refiners there is required only a careful and intelligent technical control of the preparation of the output and its application to the bleaching of oils."

The Cork Industry of Spain.

Seventy per cent of the world's cork is produced in Spain and Portugal. Consul Charles S. Winans, Seville, reports that according to the best information obtainable, there were produced in Spain during 1912 approximately 78,000 short tons of cork, of which 54,780 tons came from Seville consular district, 12,650 tons from Cataluna and Castellon, 7,110 tons from Galicia, and 3,460 tons from the two Castile Provinces. It is estimated that the cork growers received an average of $57.90 per ton for this product, or $4,516,200 for the entire quantity produced in Spain.

The finest cork is grown in various sections of the Provinces of Seville, Badajoz, Caceres, Cadiz, Huelva and Cordoba of this consular district, and in the Provinces of Gerona, Barcelona, Castellon, Ciudad Real, Toledo, Malaga, and Salamanca. The greater part of the finest cork, however, grows in the neighborhood of Barcelona, and most of the low-grade cork is produced in this (Seville) district.

In Seville district there are 305 cork factories, large and small, for the manufacture of corks and cork disks and for preparing corkwood for export; these factories are distributed in 48 towns. There are 507 cork factories in 31 towns in the Provinces of Barcelona and Gerona.

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NAPHTHALENE-FREE CARBON AND THE FRACTIONATING CONSTANTS OF COAL-TAR.

By E. C. PAILLER.*

The use of coal-tars for road binders has advanced considerably during the past few years, and many preparations of it are on the market. Many successes and failures have resulted and often no clue has been obtained as to the reason of such failures, and they were supposed to be due to the free carbon and naphthalene content of the coal-tar. Naphthalene $C_{10}H_8$ occurs in large quantities in tars. In the pure state it exists in the white crystalline masses of thin rhomboidal scales melting at 79° C., boiling point 218° C., and of characteristic odor found in moth balls. It is very volatile in the free state and has a specific gravity of 1.1517 at 15° C.

The results of the following experiments may be of interest. The experiments were made on a tar containing 4 per cent naphthalene. A mixture of fine gravel and ashes (2:1) was treated with tar and allowed to set in the open for one month. Two pieces, 5 square inches in surface and ½ inch thick, were cut out and placed in a tarred flat dish. No. 1 was kept at room temperature and the other in an incubator at 105 to 110° F. At the end of twenty-one days they were weighed.

	No. 1 Ordinary temp.	No. 2 105 to 110° F.
Total loss	1.114 grams	2.150 grams
Loss per sq. inch	0.254 grams	0.430 grams
Total loss by weight	2.07%	4.09%

An examination after the experiment No. 1 showed little naphthalene on the surface and an appreciable amount on the four sides and the underside, which had rested on the basin, was covered with naphthalene. The piece was tough and flexible; a finger-nail impression could easily be made on the surface, and on breaking it was found to be moist just below the upper surface. On No. 2 practically no naphthalene crystals were present on the top sides or underneath. The piece was tough and flexible, but not as flexible as No. 1, and it was possible to make a finger-nail impression on the top surface, but not as easily as in No. 1. In breaking it was moist and sticky just below the top surface and there appeared to be no loss of the binding properties, showing clearly that an amount, like 4 per cent naphthalene, is not detrimental to a road tar.

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DETERMINATION OF NAPHTHALENE.

The excessive amount of naphthalene in some coal-tar oils and road tars brings us to a point where it is important to decide upon a quick, but accurate, method of determining the amount of naphthalene in coal-tars. Although the picric acid methods are good ones to use, they are not always convenient, require considerable time and several chemicals. The method devised by J. C. Mann (*Journal of Chemical Industry*, June, 1910) is the quickest and most accurate method. This method depends upon the latent heat of fusion which is given off when the naphthalene and solution in the hot liquid hydrocarbons crystallize out on cooling.

FRACTIONATING CONSTANTS OF COAL-TAR.

Particular stress is laid on the fractional distillation of coal-tar oils and it is of extreme importance that the exact methods and apparatus used in the same should be specified. In order to show how important it is to specify methods and apparatus, the results of a few experiments made with a retort and two different Ladenburg flasks are given. The retort used was of the 250 c.c. size with tubulated beak 14½ ins. long, ½-in. internal diameter at the entry, and the bulb was 4½ ins. from top to bottom. Ladenburg flask No. 1 was a 200 c.c. flask, the overall dimensions 11 ins. and the two bulbs 2¼ ins. in diameter. The outlet tube was 1¼ ins. above the top of the bulbs and was ⅜-in. in diameter and connected to a glass tube ¾-in. inside diameter; 26 ins. long and acting as a condenser. The Ladenburg flask No. 2 was a 300 c.c. size; overall dimensions 19 ins; three bulbs of 2½ ins. diameter connected to a condensing tube of exactly the same dimensions as that of flask No. 1. In both cases the bulb of the thermometer was placed just opposite the outlet tube. The distance between the thermometer bulb and the top of the liquid was 5 ins. in flask No. 1 and 7 ins. in flask No. 2. The coal-tar oil had a specific gravity of 1.105 at 38° C. and was free from water and naphthalene at 60° C. Table I will show the results of the fractional distillation.

This enormous difference shows clearly how important it is to specify all details of the method and apparatus to be used in fractional distillation. It is also of great importance to regulate the speed of distillation to about one or two drops per second. The oil was distillated in the same apparatus, using a 200 c.c. Ladenburg flask, distillation No. 1 at about three drops in two seconds; distillation No. 2 at more than three drops per second with the following results:

200° C.	0.70	0.00
200-235° C.	12.76	8.40
235-315° C.	36.90	42.30

If the same method and the same apparatus are used and the distillation carried on at the same rate of speed, it will be possible to obtain uniform results.

FREE-CARBON DETERMINATION.

This determination will be only of real value in heavy coal-tars such as are used in road construction. Lighter oils, which are used in the preparation of wood blocks, contain only a small amount of free carbon, from 3 to 5 per cent, and the determination can easily be made by dissolving 5 grams in 200 c.c. of chloroform or carbon bisulphide, filtering the mixture through a tarred Gooch crucible washing with solvent until the washings are colorless; drying it at 110° C. and weighing. The amount of free carbon in heavy road tars is often as high as 23 per cent, and it would be quite impossible to filter this large amount without losing some of it or without running the risk of clogging the filter. The so-called free carbon in road tars is not pure amorphous carbon, but contains also small quantities of other bodies, and this fact has an important bearing on the process which should be used. One method used is to weigh 10 grams of the tar into an extraction thimble, closed with a cotton plug, the weight of which was previously obtained, and extracting it in a Soxhlet apparatus fifty times each with benzol pyridine bases; boiling point 140° C. unmineralized methylated stress. The thimble is then dried in a steam oven and weighed.

Another method is to weigh 5 grams into a beaker, dissolving it in 12½ c.c. benzol under constant stirring, adding 12½ c.c. hot glacial acetic acid. The mixture is stirred for three minutes on a water bath and placed in a tarred extraction thimble closed with a cotton plug and extracted in a Soxhlet apparatus with benzol until colorless, and then the carbon bisulphide until colorless. It is then dried in a steam oven and weighed.

The method which I consider the best from more than a dozen different experiments is as follows:

Ten grams are weighed into a beaker dissolved in 12½ c.c. benzol, 12½ c.c. glacial acetic acid added, and the mixture stirred for three minutes and placed into an extraction thimble closed with a cotton plug and a paper cap which were previously extracted and weighed. This thimble is now soaked in benzol for 15 minutes and extracted four times with benzol. After this it is extracted with 90 per cent cresylic acid until colorless and again with benzol until colorless. The thimble is then dried in a steam oven. This method can be carried on in one-quarter of the time than any of the others, and shows uniform results.

	Highest.	Lowest.	Average.
First method	20.92	19.40	20.16
Second method	22.87	20.62	21.36
Third method	19.35	19.19	19.25

TABLE I.

	I. Thermometer in liquid bulb ⅜" from bottom of retort.	II. Thermometer in vapor bulb just below neck of retort and ½" from liquid.	III. Thermometer in liquid bulb ⅜" from bottom of retort. Retort covered with tin hood packed with asbestos.	IV. Thermometer in vapor bulb just below neck of retort 1½" from liquid. Retort covered with tin hood packed with asbestos.	V. Ladenburg's flask No. I.	VI. Ladenburg's flask No. II.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Below 200° C.	0.85	1.20	0.20	0.50	0.80	1.10
200-235° C.	11.95	23.00	26.70	25.70	17.00	15.40
235-315° C.	31.00	12.00	22.00	25.00	25.00	24.60
Total distillate	42.80	46.20	48.90	51.20	42.80	41.10

These results speak very well for the last method as the difference between the highest and the lowest is only two-tenths of one per cent apart. Considering the short time needed and the uniformity of results, it seems that this method should be used in all determinations of free carbon.

It is not my desire to discuss the merits or disadvantages of free carbon and tars, especially the binding value. The free carbon in tars, which is washed, shows a very high cohesion and the pressure of twenty-five pounds is sufficient to compress the carbon so that it can be handled. Recently a method was patented in which the free carbon obtained from coal-tars was compressed into carbon rods which were used for the electric arc, speaking very well for the cohesion of this particular form of carbon.

British imports from the United States during the three quarters ended Sept. 30 aggregated $456,500,000.

During the fiscal year ending June 30, 1913, 839 samples of road materials were received and tested in the physical, chemical, and petrographic laboratories of the U. S. Office of Public Roads. These materials included 638 samples of various rocks and gravel and 201 samples of oils, asphalts, tars, and other bituminous materials.

ENCOURAGEMENT OF AMERICAN DEVELOPMENT.

In address before the Society of Chemical Industry, Prof. M. C. Whitaker of Columbia University, pointed out the need of a better understanding between the inventor and the investor. Inventors in almost all cases have and will continue to have poor business judgment, and investors could not by any form of training or experience be expected to exercise good judgment in matters involving fundamental, technical or engineering questions.

The first step in getting a clearer understanding of the problem of financing new enterprises is to clearly distinguish between legitimate investors and speculative investors or exploiters. The legitimate investor is interested in the underlying technical principles, the relations of the proposed development to other industries, the ratio of the capital required to the probable earnings, and the general business outlook as a basis for substantial, steady and permanent growth. The speculative investor gives little or no attention to the features of stability or steady growth and is interested in the fundamental, economic and technical questions involved only to the extent of getting a favorable report, or testimonial if you please, signed by some real or alleged expert. A laudatory report coupled with a financial set-up which makes the proposition look like a 100 to 1,000 per cent winner are the chief tools of the exploiter and the process of adding water to dissolve the imaginary profits and of letting the public in at the lower levels goes merrily on without any thought for the problems to be encountered in developing a factory and organization of permanence. Even before a site is selected and buildings erected the enterprise is swamped as a result of financial exploitation. Some new enterprises survive in spite of the exploitation practices, but in the majority of cases failure results. These failures, even though they in no way involve the soundness of the fundamental process, discredit all new developments, increase the difficulties of gaining financial support necessary for industrial growth and place the profession in an unfavorable light before the public. Meritorious inventions and legitimate business enterprises find it particularly difficult to get legitimate financial support in America because exploitation is assumed to be an essential accompaniment. Even our legitimate investors are superficial and often refuse to consider new proposition unless it can be shown that the idea has been approved or successfully applied abroad, and we are all familiar with the spectacle of meritorious American developments being compelled to depend for their financial support upon European capital.

The establishment of large factories for the manufacture of air nitrate in Norway is a development of the greatest economic importance, and has been hailed as another achievement of European chemists and engineers. The work of Bradley and Lovejoy at Niagara Falls fifteen years ago, failed for lack of financial support because our legitimate investors could not be interested in a new American development and speculative investors could not see more than 20 per cent profit. Had this enterprise been supported with half of the moral and financial backing given by European investors, air nitrate would have been a reality in America ten years before it was completed in Norway. Now that the scientific principle and the business outlook for an air nitrate industry have had the stamp of approval of Europe, our investors will no doubt look with favor upon the proposition and pay a premium for their stock.

We have just celebrated the tenth anniversary of the first aeroplane flight of the Wright brothers in Dayton. We point with great pride to our American invention and the marvelous development of aeroplanes in these ten years, but we pass lightly over the early struggles of the Wrights for financial support which was finally obtained in Europe.

The American attitude is often that of critic and doubting Thomas in regard to such new developments and is in strong contrast to the attitude of the Germans, for example, in the manner of Dr. Eyde's air nitrate, or towards Zeppelin in the development of his airships.

Our men of means do not readily support a new idea from the standpoint of its scientific interest, industrial or economic possibilities, or from motives of national pride as is often the case abroad. They do not examine our enterprises with a view to ascertaining their investment value and prospective stability, but entirely with a view to their speculative value and the possibilities of exploitation.

Many inventors have had the experience of submitting a carefully prepared prospectus showing a probable net profit of 15 to 25 per cent on the investment only to be told by the investors that they could not consider anything which indicated a profit of less than 100 to 1,000 per cent. Only propositions which hold out promise of abnormally large profits make a strong appeal for financial support and are capable of development in America.

Up to this time, the financial interests which represent real investors, favor as investment mediums the railroads, trolley lines, gas and electric companies, etc. During the period of introduction the capital requirements of these public service enterprises have been enormous, but it should be noted that the rate of introduction is rapidly decreasing and their capital needs will soon be limited to natural extensions and developments. While these channels will undoubtedly continue to absorb a large amount of capital, it is perfectly evident from the nature of inquiries now met, that investors are feeling the need of new outlets and are taking a greater interest in new industrial developments.

The first step in placing industrial propositions in a position to benefit by a more favorable investment

sentiment will be to eliminate the speculative element. Any new manufacturing enterprise has a struggle to develop plant and process and attain commercial recognition without being burdened with inflated stock issues and a heavy bonded debt on assets which do not exist. Exploitation may follow development but should not be permitted to anticipate it.

Investors must be convinced that there is an accurate and available way to evaluate an industrial proposition just as there is for a railway or a lighting plant. At the present time a report from an auditor or a "certified public accountant" seems to enjoy the highest favor as a means of determining the value of an industrial property. Just how the books of a concern are going to show the physical condition of a property, the workability of a process, the general efficiency of the plant, the state of development of an organization, or the general business outlook is not clear. When it comes to estimating the value of a proposition involving the applications of chemistry, all experts look alike to the investor and the report of an expert accountant is as impressive and more intelligible to him than that of a chemist or chemical engineer. Is it any wonder, when intelligent and conservative investors fail to distinguish between proper and improper advice on which to base their investments, that the unthinking public should be victimized by Keeleys, Cooks and Friedmans?

Great responsibility will devolve upon the advisory expert who investigates and recommends new propositions. His position is an important one because ultra-conservatism leading to a rejection of an opportunity would be as unfortunate as an overoptimistic view which would result in illadvised investments.

It is evident, therefore, that men of experience and judgment in the industrial field and particularly the industries involving chemistry, will be called upon to perform an increasingly important function in industrial development. Investigators will require not only a knowledge of the scientific principles involved in the proposed industry, but a knowledge based on experience in actual manufacturing propositions and processes, a knowledge of business and competitive conditions, a knowledge of the labor problems involved, a knowledge of costs in accounting and, most important of all, a broad comprehensive view of the general industrial outlook. Impending competition from other sources, impending improvements in processes of manufacture or production, transportation advantages, market fluctuations and innumerable other conditions will also have to be considered. In this capacity the chemical profession will be called upon to perform a broader function than heretofore, and its work will be more important than that covered by the usual interpretation of the term "consulting chemist."

The fiber division of the Bureau of Agriculture at Manila is conducting extensive tests to establish scientific standards for the Philippine fiber production.

COAL-TAR AND ASPHALT PRODUCTS FOR WATERPROOFING.*

By S. T. WAGNER.

The increasing number of solid-floor bridges, especially in cities, involving waterproofing and the expenditure of large sums of money, and the necessity of thoroughly protecting steel reinforcement in concrete under certain conditions, as well as the waterproofing of masonry in general, make the study of the various external methods of waterproofing of the greatest importance. The methods referred to consist in the application to the surface to be waterproofed of either a membrane of felt or fabric of some kind thoroughly cemented together with some bituminous material, or a layer of inorganic material impregnated with the same substance.

There can be no question but that the bituminous material so used is the real waterproofing medium, and that all other materials incorporated therein are simply fillers to retain the bituminous material in place and give it additional reinforcement of some kind.

Whether the waterproofing is applied for the protection of the public from drippings from an overhead railroad bridge, or is used to prevent the corrosion of reinforcing material in concrete construction exposed to water, the object in either case is to obtain a layer of durable waterproofing material which is suitable to each particular case.

Waterproofing is expensive; it is always very difficult and costly to repair if defective; and it behooves the engineer to use the best materials that he can secure and to supply them with the greatest care to the structure, which should be especially designed to meet the necessary details required in good waterproofing practice. There is much uncertainty at the present time as to a number of points in connection with this character of work, but there appears to be almost complete agreement that the perfect or imperfect application of the materials determines a good or a bad piece of work.

It would appear that, outside of particular instances where waterproofing is used to keep water in, the majority of cases are those in which the object is to keep the water out; and of these a very considerable portion of the structures requiring its use are essentially different as indicated above—first, solid-floor bridges; second, underground masonry.

In the first case the conditions are such as to require special elasticity at all temperatures in order that the waterproofing may adjust itself to the vibrations of the structure, especially in the cases of railroad bridges of relatively short span. It is usual to have a regularly ballasted floor, which if properly drained make a condition for which we can say in general that the oxidizing action of the air is probably a more potent factor in the disintegration of the

*Paper presented at 16th annual meeting of American Society for Testing Materials.

waterproofing material than the action of whatever water may be present.

In the second case we may safely say that when the masonry is covered with even a small amount of earth, the action of the air is negligible and that of the dampness, or water, is the more serious. In some instances water may be in constant contact with the waterproofing.

The materials to be used should therefore have chemical and physical characteristics which make them suitable for the above-mentioned conditions.

There are in use at the present time two general classes of materials which are used for waterproofing purposes when the conditions are as just described. First, compounds of an asphaltic nature; second, coal-tar pitch. Both of these materials have been and are at present used quite extensively and with varying success. The successes or failures in many cases have been due to proper or improper application as much as to the inherent qualities of the materials themselves; and it is believed that the successful use of either class has often been attributed to this fact rather than to the real qualities of the materials, and that at the present time the amount of reliable data as to what is needed in the way of a specification for the proper material to be used is woefully lacking.

To one who is not a modern chemist and thoroughly versed in the mystic symbols of the hydrocarbons, the chemistry of these materials is almost hopeless in its practical application; but it is quite evident that there is an essential difference between them chemically, that is, between such figures as are usually given in chemical analyses.

The physical properties are apparently much more interesting and useful to the practical engineer, and it would seem we could do away with the chemical data unless they indicate properties which when translated will enable us to distinguish undesirable, or it may be dangerous, elements. We can understand and appreciate such figures as melting point, brittle point, elasticity at various temperatures, and consistency, and data concerning these properties give us a very fair idea of the various physical properties.

The data which seem to be needed are those from laboratory tests which will enable us to determine the relative durability of these products, first, when exposed to the air; second, when exposed to water, and third, when alternately wet and dry. Any such test is, or would be, essentially an accelerated test. It is possible that at the present time the question of durability might have to be answered by practical experience with the different materials in existing structures. However, it does seem that some information as to what we should aim for and what should be avoided is due from the manufacturer or the chemist. Nothing inspires the confidence of the user of a structural material so much as the free discussion of the methods of manufacture on the part of the manufacturers. Experience in the past with other materials has shown that this confidence is not abused in the preparation of specifications. Such information is badly needed in connection with waterproofing materials.

From recent investigations and research there seems to be a general impression that when exposed to the air, asphalt products are more durable than coal-tar products, and that the opposite is true when exposed to water. The opinion that asphalt products are more suitable for use on solid-floor bridges seems to be of general though not universal prevalence, on account of the greater elasticity of this material at low temperatures. In other words, an asphalt product with a melting point of 150° F. which will be ductile at a temperature of 40° F. or lower can be obtained, while a coal-tar pitch with the same properties can not. It has been the experience of the writer that asphalt mastics made with natural rock asphalts, when fluxed with asphalt compounds of high ductility at low temperatures, produce mastics which are much less liable to crack in service than are those in which the flux used is brittle when cold.

Water to a certain extent is a solvent of all asphalts, but from the tests of Whipple and Jackson[1] it is quite evident that the question of solubility is a comparative one, and the tests there given show that there are classes of asphalts upon which the action of water is very slight. In this paper a quotation is made from Richardson[2] which shows that the action of water upon coal tar is about two-thirds of that upon Bermudez asphalt cement when expressed as the gain in weight in water in a given time. Bermudez asphalt is the tests made by Whipple and Jackson is among those which were most affected by water. A number of cases of the durability of coal-tar pitch in actual service in underground work seem to indicate very positively its suitability for this class of work. Will some one say whether or not properly selected asphalts are unsuitable under similar conditions?

Apparently the questions which need to be answered are the following:

1. What kind of materials are most suitable for general application to (a) solid-floor bridges; (b) underground masonry?
2. What kind of materials are most durable for (a) solid-floor bridges; (b) underground masonry?
3. If asphalt products are used, what should be specified?
4. If coal-tar products are used, what should be specified?

Probably the answers to these questions belong to the work now under consideration by Committee D-8 on Waterproofing Materials, but a general discussion of the subject may be of material assistance to the committee in its work.

[1] Proceedings, Brooklyn Engineers' Club, March 8, 1900.
[2] Municipal Engineering Magazine, June to August, 1897.

A MODEL GARBAGE INCINERATION PLANT.*

By CONSUL GEORGE NICOLAS IFFT, Nuremberg, Germany.

Furth, a Bavarian city of 70,000 population, a suburb of the city of Nuremberg, has had in operation for more than two years a municipal garbage incineration plant that is regarded as a model of its kind and which, in connection with a modern system of garbage collection, makes the disposal of garbage of that city not only the least offensive and most sanitary possible, but also a matter of actual, although small, profit to the municipality. Other German cities have excellent garbage incineration plants and still more almost ideal systems of collecting the garbage, but Furth is unique in that it combines the two and that both are models of their kind. The Royal Bavarian factory inspector, after a recent survey of the plant, states in his report:

> The visit at the garbage incineration plant showed that, in a model manner, through avoidance of sorting and piling up of the garbage on the premises, through delivery in completely closed boxes, prevention of any possible dust and escape of gases by dumping into the furnace, cooling of the slag in a special chamber, segregation of the floating ashes, and removal of the hot gases in a chimney 50 meters (164 feet) high, ample provision has been made for preventing any damage to the surroundings.

The garbage incineration plant occupies an oblong building 50 by 20 meters (164 by 65.6 feet) ground plan and is located on the outskirts of the city, on the same premises with the municipal gas works. The building contains the boiler plant of the gas works as well as the incineration furnace.

COLLECTION OF THE GARBAGE.

Until the garbage incineration plant was put into operation in February, 1911, Furth disposed of its garbage in the old-fashioned manner—it was deposited in receptacles of all descriptions, mostly uncovered, and placed in front of the houses for transportation to the dumping grounds. The collection wagons were simple carts with lids. There was nothing to prevent the dissemination of dust and stench in loading and unloading or even in transportation. The dumping ground lay in the vicinity of dwellings, into which dust and stenches were continually blown, and was, in spite of police prohibition, visited by small children and that class of people who always searched garbage heaps for scraps.

The city magistrates on Nov. 24, 1910, passed an ordinance requiring all persons living within the garbage-removal district to put household and kitchen waste, sweepings, ashes, and similar materials (excepting tin, wire, and metal scraps, glass, porcelain, and clay vessels) in cans to be provided by the municipal incineration plant. The single-can system was adopted—one can for each household—and a can of such limited dimensions that the public would not be tempted to throw old shoes, dilapidated hats, and broken pots in the same vessel with garbage proper.

Each household must use the can furnished by the city. It is made of sheet iron with a heavy coating of zinc and has a capacity of 33 liters (8.7 gallons). The cans are solidly made, have a flat sliding lid fastened with a bolt, and can be conveniently piled on top of each other. The cans are known as the "Ochsner system" and those in Furth are manufactured at Weidenau an-der-Sieg and at Lauterbach in Hessen.

DESCRIPTION OF WAGONS USED FOR COLLECTING GARBAGE.

The wagons, another feature of the collection, consist of a long truck on which rest four box segments divided into two compartments and opened at the top by sliding lids. There are eight such lids on each side of the wagon. The garbage can is placed top downward on one of these lids in such a way that a device in the can lid catches on a rod extending along the edge of the segment box. This movement pushes back the lid of the wagon and opens the can, for the can lid remains attached to the rod. The garbage falls unseen, without dissemination of odor or dust, into the wagon. Each segment box has a capacity of 1.7 cubic meters (2.2234 cu. yds.), consequently that of the wagon is 6.8 cubic meters (8.8937 cu. yds.). The average weight of the garbage in each wagon is 2,550 kilos (5,621.8 lbs.). The sliding lids on the boxes are 1.45 meters (4¾ ft.) above the ground, permitting the collector to stand conveniently on the pavement and empty the cans. These boxes are removed from the wagon truck one at a time by an electric crane and placed on top of the furnace, into which the contents go upon opening a spring valve in the bottom.

The garbage wagons are so constructed that they may be driven by horses or by mechanical power. Experience has proven the latter to be 36 per cent cheaper than the former. The wagons, therefore, are ordinarily coupled to an electric automobile having two large driving wheels in front and two smaller wheels in the rear, which are hoisted about a foot above the ground when the automobile is attached to the wagon and lowered only when it is detached. The axle motors (Braun system) have an efficiency of 5.15 h.p. and are operated by storage batteries charged at the power house of the municipal electric works. They are divided into 42 cells and have a capacity of 390 ampere hours. The automobiles, when attached to the garbage wagons, attain a speed of 2 to 14 kilometers (1.24 to 8.7 miles) per hour, and when attached to the city supply wagons can reach 24 kilometers (14.9 miles) per hour. The trucks of the garbage wagons rest on two pairs of wheels, making three pairs in all when the automobile is attached, and are so adjusted that both can be turned in a surprisingly small space.

The wagon trucks as well as the detachable boxes

*From Daily Consular and Trade Reports.

are manufactured in Furth and Nuremberg. The automobiles are made exclusively in the latter place. The storage batteries are made in Berlin.

THE INCINERATION PLANT.

After the city decided to burn its garbage it made a careful investigation, finally deciding on the type of furnace (the "Humboldt system") used at Barmen as the one giving the most satisfactory results. The one at Furth is a cubic mass of brick, about 16 feet in dimension, and is divided into two chambers. Into these the two compartments of the garbage box are successively emptied after the latter has been hoisted from the truck by a crane and placed on top of the furnace. This is accomplished invisibly and there is no exhalation of any kind, because a system of mechanical draft creates a powerful suction. The wagon could be drawn directly onto the furnace without a pulley if the necessary structure were present, but the city uses the present apparatus for reasons of economy, as it did not wish to incur too great an expense in remodeling the old plant.

The garbage thrown into the furnace comes in contact with the hot walls and the glowing slack and ignites in a few minutes. The furnace grates are divided into two parts—a principal grate and a front grate. Air is introduced through numerous holes in the grates by a turbine draft, manufactured at Aerzen-Hameln. The garbage is first dumped onto the principal grate, where it burns at an average rate of 1 cubic meter (1.3 cubic yards) in 15 to 30 minutes, the time depending on the amount of moisture in the garbage, and being longer in summer on account of the larger masses of vegetable waste. After the garbage is burned to a slack it is pulled with long hooks, operated by hand, onto the front grate, where it remains until the next wagon load is dumped into the furnace. It keeps the furnace warm and helps destroy the gases from the garbage being burned on the principal grate.

The gases are withdrawn into a separate chamber, where a temperature of 1,200 to 1,400° C. destroys all organic and unwholesome materials, and where the floating ashes are segregated. They then pass to a boiler with a heating surface of 220 square meters (2,368 sq. ft.), which they touch on the front wall and then on the back wall, after passing beneath through pipes. The floating dust and ashes that still remain in the gases are precipitated under the boiler. The gases so purified now escape from chimneys 50 meters (164 ft.) high. The ashes that accumulate in the pipes and under the boiler are pumped out automatically by rotation pumps manufactured at Nuremberg. The steam generated in the boiler is used primarily in the gas plant and what then remains is converted into electricity and used in the electrical plant.

The garbage is burned into a mass of slack, which is removed from the front grate into iron carts with long hooks operated by hand. The slack is cooled in water and then removed to a crusher, where it is pulverized. Hard substances, like pieces of metal, which were not decomposed in the heat of the furnace, are here separated. The ground slack is sifted into two piles, the one fine as gravel and the other about as coarse as chestnut coal. The ground slack has been pronounced by eminent authorities an excellent substitute for the gravel ordinarily used in mixing concrete (Beton).

COST OF REMOVAL SYSTEM—AMOUNT REMOVED.

In the municipal ordinance of November 24, 1910, referred to, it was provided that all garbage must be placed in receptacles to be furnished by the municipal garbage removal bureau. The distribution of garbage cans began in January following, and by the end of February, 1911, about 1,500 cans had been distributed. At the end of the year this number had increased to 16,017. About 85 per cent of these were sold for cash at 3.75 marks (about 90 cents) per can, and the rest were paid for in 24 monthly installments of 20 pfennigs (4¾ cents) each. The old receptacles were used until the distribution of the new cans was effected.

The city began to remove its garbage in the new manner in the latter part of February, 1911, after the incineration plant went into operation. It had at its disposal three electric automobiles, three wagons, one supply wagon, and forty-four detachable garbage boxes. The total cost of installing this garbage-removal system was $10,888. Each wagon is accompanied by four to five men, who fill it in less than an hour. The electric automobile that hauls it to the incineration plant is immediately attached to a wagon that has been emptied in the meanwhile and returns to the place of collection. During the 11 months of operation in 1911, 1,873 collection trips were made, totaling 2,253 hours, i. e., each wagon was employed in collecting on an average of 1.2 hours per trip. During the same year a total of 10,517,000 lbs. of garbage was so collected. The total distance traveled by all the wagons was 8,456 miles. At the same time a smaller quantity was collected and transported in wagons drawn by horses, the average time taken by each wagon in this case being 1.46 hours. The amount of garbage brought to the plant in this latter manner amounted to 427,344 lbs., making a grand total of all garbage collected by means of horses and automobiles of 10,944,344 pounds.

EXPENSES AND RECEIPTS OF COLLECTING DEPARTMENT.

On one day in the week in summer and on two days in the week in winter garbage is collected by horsepower, but only two segment boxes are used in this case, instead of the four used when the delivery is made by automobiles. The garbage collected in 1911 came from 2,255 properties, with a population of about 63,400. The whole business of collecting requires only ten persons, namely, a foreman, a preparer, four collectors, two automobile drivers, and two assistants. In winter an extra collector is employed.

The cost of collecting the garbage in 1911 was covered almost exclusively by fees taken from the property owners in the collection district. The amount of the fee is based on the rental value of the rooms from which the garbage is collected as ascertained in the tax valuation. As a rule the rental value of all the rooms is taken into account, but certain exceptions are made, as, for instance, when continuously for more than six months no garbage has been collected from certain parts of the building. The total sum derived from fees in 1911 was $9,044. The cost of administration during the same year amounted to about $595, and the cost of operating to nearly $5,236.

Before the furnace was installed it was calculated that the annual quantity of garbage to be collected in Furth would amount to 12,000 tons. This computation rested on statistics from other German cities, where the daily output of garbage is 1.1 pounds per capita. It was found, however, that the total amount actually collected at the end of the year was less than 5,000 tons. The average time spent daily in consuming the garbage was 11.7 hours, so that the furnace cooled in the meanwhile, requiring considerable waste of time each morning to bring it to the normal temperature.

The furnace, as stated, is divided into two chambers and there is a supplementary chamber for burning coke. This was designed to supply steam for the gas works during the night, when the garbage furnace was not in operation, but it was soon found to be inefficient for the purpose, and will probably be converted into a garbage furnace. Each chamber in 1911 received 7,544 dumpings, each representing the contents of a segment box holding 1,400 to 1,500 pounds of garbage. The average time spent in burning each load was 24.6 minutes.

The steam generated in the boiler is used mainly in the gas works and the remainder is converted into electricity. In 1911 nearly 6,540 cubic yards of water were turned into steam. It is the most important item in making the incineration plant a profitable undertaking. For 1911 the value of the steam generated was estimated at about $5,700 and the price received for the slag was only $714. The expenses of operation for the same year were: Salaries and wages, $2,451; use of water, $714; maintenance, $536; interest on loan, $762; depreciation, $1,785. The income from the value of steam and the sale of slag was $6,414, leaving a slight profit of $166.

CHARACTER OF THE SLAG.

The only product of the garbage incineration presenting commercial possibilities is the slag. It was first used to cover the old dumping ground and then employed in concrete structures on the premises. Several authorities have carefully tested it and pronounced it an excellent substitute for the gravel ordinarily employed in mixing concrete. In some of the strength tests of the former, concrete cubes made of slag showed a resistance of 175 kilos per square centimeter (2,489 lbs. per square). In the freezing tests, which lasted 21 days, the cubes were submitted to 25 alternate freezings and heatings, but at the end of this period their condition was unchanged. Other tests made were even more favorable, showing a resistance as high as 302 kilos (666 pounds) per square centimeter. Inasmuch as the minimum resistance required of concrete pillars and foundations is only 80 to 100 kilos, the value of the slag is apparent. The chemical analysis of the slag gave the following result:

Constituents.	Per cent.
Silicic acid, SiO_2	53.38
Lime, CaO	6.48
Oxide of iron, Fe_2O_3	19.62
Alumina, AlO_3	11.08
Magnesia, MgO	1.20
Sulphuric acid anhydride, SO_3	.28
Phosphorus pentoxide, P_2O_5	1.52
Alkali residue	5.54

Up to the present the city has sold the coarser grade of sifted slag for 4.50 marks per cubic meter ($0.824 per cu. yd.), but has used all the finer sort on the premises. It hopes in time to derive considerable profit from the sale of slag.

SYSTEMS IN OTHER GERMAN CITIES.

Furth is the only city in Germany that combines the two systems above mentioned. The Humboldt furnace was first introduced at Barmen and is being installed in other Continental cities—Frankfort-on-the-Main, Altona, Kiel, Wien, etc. Zurich has an incineration plant, but uses an English type of furnace, and so did Hamburg until it recently adopted a system of its own, which can only be used in burning the garbage found at a seaport. The Humboldt furnace has recently been introduced into Brazil. The Ochsner garbage cans and the garbage wagons are not in general use, except at Furth. Berlin, with its 2,000,000 inhabitants, still collects its garbage in the old manner and has no incineration plant. The sewage of Furth is still disposed of in the primitive way; that is, it is dumped into a little stream known as the Rednitz.

As already noted, the small garbage cans are not destined for the reception of scrap tin, old shoes, etc. These, however, are also carted away in separate wagons free of charge, are sorted at the garbage plant, and the scraps are sold, producing enough to pay for their removal.

At the Leeds Leather Fair, Oct. 29 last, Vice Consul Charles E. Taylor reports that "there was much inquiry from America for samples and prices of sole and upper leather, and good business is expected."

A monograph entitled "Edible Oils in the Mediterranean District," prepared by Commercial Agent Erwin W. Thompson, has been issued by the Bureau of Foreign and Domestic Commerce. This monograph is especially concerned with the seed-oil industry of Marseille, the chief crushing center of the world.

PRODUCTION OF HYDROGEN FROM WATER AND COAL FROM CELLUSE AT HIGH TEMPERATURES AND PRESSURES.*

The progress of chemical knowledge has very often been caused by the progress of experimental possibilities and the improvement of experimental methods. Thus the chemistry of high temperature grew up after the introduction of electrical methods into the chemical laboratory. By electrical methods chemists were enabled easily to produce high temperatures. At the same time the electrical and optical methods of measuring these temperatures were so much refined that the handling of high temperature experiments ceased to be a difficult task.

The laboratory results were soon made use of in technical work and now we have a large industry, based upon the methods of electrical heating.

If we adopt this methodical point of view it will be observed that there is noticeable progress in every science, whenever new methods and a new instrument is introduced. I may refer to the combustion furnace in organic chemistry, to the optical methods, refractometry and spectroscopy, to the measurement of electrolytic conductivity, to the method of producing high temperatures, to the liquefaction of gases and the production of low temperatures. One of the most recent methods introduced into the laboratory is that of handling very high pressures conveniently and without danger.

It is this subject to which I wish to call attention here, not merely because some very promising results have been obtained already during the last few years, but also because I am convinced that many important results will be obtained through this experimental method.

Chemical reactions under pressures higher than that of the atmosphere are not unknown in the laboratory and in chemical industry, but these efforts are characterized by their purely qualitative nature and the limited extent to which the pressure could be raised. The former was due to the lack of appreciation of the extent to which chemical reaction may be influenced by pressure, and this in general led to a mere attempt at raising the temperature of a liquid component of a chemical reaction above its boiling point. The second restriction lay in the inadequacy of technique and in the construction of the retaining vessels.

Now the principles of modern physical chemistry teach us that besides this application of pressure so often employed there are other ways of influencing chemical reactions by means of pressure. For instance, the law of mass action tells us when and in what direction an equibrium will be changed by an increase of concentration, that is of pressure of any one component of a chemical reaction. Leaving aside reactions in condensed systems, that is in the liquid and the solid state, there remain those reactions with gaseous components which are most easily affected by pressure.

Momogeneous gaseous reactions under the influence of pressure are forced in the direction in which a reduction of the number of molecules takes place. A chemical reaction can therefore be carried further by an increase of pressure whenever the reaction is accompanid by a diminution of volume.

An excellent example of this sort is the synthesis of ammonia from its elements. A glance at the equation, $N_2 + .3H_2 = 2HN_3$, shows that four molecules of the mixture of nitrogen and hydrogen give two molecules of ammonia. The reaction thus leads to a diminution of molecules or a decrease of volume. The formation of ammonia must therefore be carried further by increased pressure. The utilization of this fact made possible the technical method of synthesising ammonia from its elements. This achievement of highest economic value was obtained by the extraordinary and systematic researches in high pressure work carried out by Haber and LeRossignol.

It may suffice to mention that this reaction is carried on at about 200 atmos., and at temperatures between 500°-600° C. in order to show that an entirely new experimental method had to be worked out. The many difficulties were overcome mainly through the extraordinary skill of Le Rossignol. Today this process has left the experimental stage and is in the hands of the Badische Anilin and Soda Fabrik, by which it has been developed into a very large industry.

When a gas enters into reaction with a liquid or a solid with the formation of a new liquid or solid substance, it is evident that pressure must again further chemical combination as predicted by the law of Le Chatelier. Heterogeneous reactions under very high pressure have not yet been used on the large scale, but according to my own results it is possible to effect, for instance, the oxidation of calicum oxide to peroxide by means of gaseous oxygen. At atmospheric pressure no appreciable reaction takes place, not because reaction cannot take place, but simply because the speed of reaction is far too slow. Reaction velocities increase with higher temperatures, but at the same time the dissociation increases also. Now by subjecting lime in fused sodium hydroxide to the action of oxygen under pressures above one hundred atmospheres, it was possible to cause formation of the peroxide from ordinary limestone.

The dissociation pressure, that is the pressure of oxygen given off by the peroxide or pressure of oxygen remaining during the action of this gas on the oxide, was measured at various temperatures. The equilibria could thus be determined and were found to coincide by both methods. At temperatures at which the reaction velocity had sufficiently increased as to become measurable, for instance at 300° C., the

*From Journal Society of Chemical Industry.

pressure of oxygen was found to be 130 atmospheres. This is the pressure of oxygen necessary to cause the gas to combine with solid calcium oxide and to convert the latter completely into peroxide. Other examples of similar reactions were found in the extensive researches of Ipatiew on the hydrogenation of various organic compounds in the presence of catalysts at high pressures. He was able, for example, to obtain alcohols from ketones and hexadydroaniline from aniline. He also succeeded in displacing some metals from aqueous solutions of their salts by hydrogen under pressure. Thus copper, silver, and mercury were precipitated from solutions of their sulphates under 100 atm. with formation of sulphuric acid, and so forth.

A third possibility of the application of high pressure for promotion of chemical reaction lies in the ability to retain the liquid state from the boiling point up to the critical point. The physical properties of a liquid may therefore be utilized at high temperatures, and thus reactions be caused to take place which at low temperatures cannot be carried out. Furthermore, the physical properties of a liquid may undergo remarkable changes between the boiling point and the critical point, as for instance the electrolytic dissociation of water. According to A. A. Noyes the dissociation of water increases between these temperatures nearly 2,000 fold.

This suggests that water must act as a fairly strong acid or base at high temperatures provided it is kept in the liquid state. In the presence of a metal we may expect therefore a reaction with evolution of gaseous hydrogen. Lead by this assumption, I have undertaken in collaboration with my assistant, Herr Specht, a series of experiments on the action of liquid water in metals, particularly on iron. The results have been very gratifying, for we believe to have found in this reaction a basis for a new technical process of generating hydrogen.

Since iron and water are the sole reacting substances, it is evident that it is possible to obtain an extremely pure quality of gas, mainly because the dangerous impurities, carbon and sulphur compounds of iron, are practically not attacked by the acid water. The gas has been analyzed and has proved to contain more than 99-95 per cent of hydrogen. Thirty liters of gas were passed over heated copper oxide in a combustion tube, the water was condensed, absorbed in drying tubes and the carbon dioxide formed absorbed in the usual way, care being taken to move all possible carbon dioxide from the condensed water.

In a second experiment, 200 liters of hydrogen were passed, under pressure, through a copper coil cooled with liquid air. The condensed fraction was driven by vaporization into a gas burette, measured and analyzed for CO_2 Co, saturated and unsaturated hydrocarbons. The analysis was as follows:

	Per cent.
Hydrogen	99.9495
Carbon monoxide	0.0011
Saturated hydrocarbons	0.0416
Unsaturated hydrocarbons	0.0078

The speed of reaction naturally depends on the temperature, but it is also affected by the presence of electrolytes such as sodium chloride, ferrous chloride, and so forth. The presence of a noble metal also accelerates the attack of the iron.

This is shown by the following table:

	Temp.	Quantity of hydrogen per hour.
Iron and pure water	300°	230
Iron and pure water $FeCl_2$	300°	1390
Iron and pure water $FeCl_2$+Cu	300°	1930
Iron and pure water Fe Cl_2+Cu	340°	3450

This table shows that the reaction increases with the increase of temperature. Within the limits practically obtainable, the speed of reaction is so great, that in a retaining vessel of ten gallons capacity about 3,000 cubic feet a day may be generated. A great advantage of this method lies in the fact that the hydrogen is at once under high pressure and may be filled into cylinders without previous compression. It is evident that between the generator and the steel bottle in which the hydrogen is collected a reflux condenser must be used in order to condense the water.

It is, furthermore, of the highest importance that the oxidation of the iron does not take place merely on the surface but penetrates the iron and oxidizes it quantitatively to Fe_3O_4 according to the equation.

$$3Fe + 4H_2O = 4H_2 + Fe_3O_4.$$

The latter is precipitated as a finely divided powder readily reducible by carbon or carbon monoxide.

The oxidation product can therefore be regenerated and re-enter the cycle process. This reduced the total expense of the process to that of the reduction of Fe_3O_4 and the energy required for heating the reacting mass with mainly liquid water to about 300°.

Compared with the latest and cheapest technical process, that of Linde-Frank-Caro, which separates hydrogen from carbon monoxide by liquefaction of carbon monoxide and other impurities of water gas, this new method offers the advantage of producing a very much purer gas without cost of purification, without cost of compression, and without any movable parts in the apparatus. The total energy expended is derived from coal, of which only about 60 per cent is needed in comparison to the Linde process. Finally, the apparatus is not only much cheaper but requires less space for the same output. Our first experimental plant in Hanover has a capacity of about 1,000 cu. ft. an hour generated in six high pressure vessels of about 10 gals. each.

As I have mentioned before, it is possible to retain under pressure a substance in the liquid state far above the boiling point. The physical properties of the liquid state can thus be made use of at high tem-

peratures. Now one of the most prominent physical properties of water in the liquid state is its very large heat capacity and heat conductivity. If, therefore, we surround with water a chemical substance undergoing chemical reaction with evolution of heat, we are able to prevent superheating of the substance. This affords a means of conducting an exothermic chemical reaction at a definite temperature without local superheating and uncontrolled decomposition at undefined temperatures.

A process of decomposition occurring every day in nature on the largest possible scale is the decomposition of cellulose. This reaction is exothermic, giving off a large amount of heat. According to our own experiments the reaction involves 70,000 grm. calories for each grm. mol. of $C_6H_{10}O_5$. This heat would suffice to raise the temperature of the reacting mass to about 1200° C. provided none of the heat could escape. In nature the velocity of this reaction is so slow, that complete decomposition of cellulose in the form of wood or peat or similar products requires geological epochs till the end product of this process, our natural coal is formed. Consequently the heat envolved during the reaction is conducted off quickly enough not to permit a noticeable rise of temperature. Every attempt to transfer this process of nature to the laboratory for thorough study means that this reaction is made to take place in hours or days, for which nature can afford to take millions of years. The speed of reaction is easily increased by allowing the reaction to run at higher temperatures, but the large amount of heat generated in so short a time has always caused superheating, which in turn leads to a more or less complete change of coal into coke. This has been the stumbling block of all previous laboratory attempts to obtain from natural products containing cellulose a substance whose chemical and physical properties are identical with those of natural coal.

If we leave out of consideration those grades of anthracites which have an extraordinarily high carbon content, we may say that coal calculated free of ash has a hydrogen value of not less than 4½ per cent. All artificial products of which analyses are at hand show a much smaller hydrogen percentage. This means that a secondary reaction has set in through which the coal has been partly changed into coke.

	Carbon, per cent.	Hydrogen, per cent.
Natural bituminous coal	75 to 90	4-5 to 5
Bergius and Specht	74-3 to 85-2	4-5 to 5-2
Stein	81-3	3-8
Klason	82-5	4-1

This table gives a summary of recent experiments in this line. In spite of various precautions for prevention of superheating, no one has succeeded so far in obtaining a product with sufficiently high hydrogen percentage.

The equipment of our high pressure laboratory suggested to us the possibility of eliminating this source of error by allowing the reaction to take place in water kept in the liquid state by means of high pressure. Water penetrating the reacting mass must, on account of its high specific heat, serve as an excellent thermostat and prevent completely the dangerous local superheating in consequence of its good conductivity. A further great advantage for the study of the reaction itself lies in the absolute constancy and definiteness of the temperatures in question throughout the whole mass. We are thus able to study the reaction at any desired temperature.

When subjected to this reaction at 340° for about twelve hours, pure cellulose yields a black powder which proves to be soft coal of about 84 per cent carbon, 5 per cent hydrogen and 11 per cent oxygen. At the same time carbon dioxide is evolved and is found under compression in the reaction vessel.

The proportion of substances found allows us to formulate the reaction about as follows:

$$4C_6H_{10}O_5 = C_{21}H_{16}O_2 + 3CO_2 + 12H_2O.$$

The heat of reaction can be calculated in the ordinary way and proves to be about 70,000 cal.

EXPERIMENTS ON FORMATION OF COAL.

Material.	Temp. °C.	Duration, hours.	Analysis of coal: C. per cent.	O. per cent.	H. per cent.	N. per cent.
Peat, original dry subst.	...	..	52.4	41.4	5.50	0.70
"	250	8	74.3	19.4	5.20	1.07
"	300	8	77.0	16.9	5.00	1.07
"	340	8	81.2	13.3	4.65	0.89
"	340	24	84.0	10.4	4.62	0.95
"	340	61	83.5	11.0	4.60	0.97
Cellulose	310	64	83.7	10.9	5.40	...
"	340	8	83.1	11.7	5.20	...

The table shows that the carbon percentage rises with the length of heating and the temperature at which the reaction takes place. It reaches, however, a final value at about 84 per cent carbon, beyond which it does not go, even after very prolonged heating. This substance therefore represents the stable end product of the voluntary reaction of decomposition mentioned above. Every further increase in the carbon value of natural coal cannot represent a further decomposition caused by the same reaction in still greater periods of time. This reaction evidently stops at this point, and only through reactions caused by new external conditions can the carbon percentage still further be raised.

What has been said of cellulose is equally true of natural products containing cellulose, such as peat or wood and so forth. The chemical structure of the carbonaceous product is hardly affected. With an increase of bituminous matter the gas shows increasing amounts of methane, and the coal some additional hydrogen.

As mentioned above, the experimental methods employed allow not only an excellent regulation but also a variation of temperature. It was therefore of interest to study the speed of the reaction at various temperatures in order to calculate from them the rate at which the reaction takes place in nature. Of course, the range of temperature in which such parallel de-

termination is possible is naturally restricted. We have carried them through at 310° and 340° C.

The end product in both cases, whether heated for 64 hours at 310° or for 8 hours at 340°, is nearly identical according to the analysis.

A rise of temperature of 30° has accelerated the reaction eight times. Eight is two to the third power, an increase obtained in three times ten degrees rise of temperature. Consequently an elevation of ten degrees approximatly doubles the speed of the reaction. This is the normal temperature co-efficient of a purely chemical reaction. Accepting this coefficient for our reaction, we are able to calculate approximately how many years were required for the conversion of peat into natural coal.

On the assumption that the reaction took place at a normal average temperature of 10 degrees centigrade in accordance with the generally accepted theory of Potonie we may say that for the formation of coal 87 per cent carbon 233×8 hours is the time required in nature. This is easily calculated to be about 8 millions of years. I give this figure with all due reserve, but it is probably correct as far as the order of magnitude is concerned.

Our geologists calculate this period to be several millions years, which is a good agreement with the results of our chemical method.

Now the product obtained by this method has all the chemical properties of natural coal. The analysis shows that it has the required composition, and furthermore all the qualitative reaction demanded by Donath for fossil coal (Steinkohle) are found to be fulfilled. The physical properties, however, differ widely from what we expect from natural coal. The new product is a very finely divided blackish powder easily suspended in water. When heated to higher temperatures it resembles a high grade of soot and might be used as a pigment.

It is, however, not impossible to convert this finely divided powder into a substance with all the physical properties of natural coal. This may be accomplished by a process most likely analogous to that used by nature. It consists not only in heating the coal powder to temperatures above 300° but subjecting it at the same time to extremely high pressure, far beyond the few hundred atmospheres required during the reaction of carbonization. Both factors seem to be of equal importance, since at ordinary temperatures even the highest pressure at our disposal, about 5,000 atmospheres, have not been able to modify the chemical composition of the powder. To be sure, there results a coherent mass with the outer appearance of coal possessing the proper specific gravity, but the chemical analysis shows that the carbon content has not changed. If, however, the temperature during compression is again raised sufficiently high to allow chemical processes to take place within a few hours, which was merely a means of accelerating in the labmillions of years, that is, if we raise the temperature during compression to about 340°, an entirely different product results. We assume in this case that the extremely high pressure forces the substance to undergo a new reaction, which has nothing to do with the reaction of carbonization found before to run on its own accord in the laboratory as well as in nature. The new reaction raises the carbon value of the coal, causing it to resemble more and more the natural anthracite, with strata at right angles to the direction of compression and with specific gravities increasing according to the temperature employed and the duration of compression.

Leaving out the effect produced by temperature, which was merely a means of accelerating in the laboratory the slow process of nature, we find for the effect of pressure perfect analogy in our natural coal fields. Whenever we find that coal field has been subjected to a compression as a result of an upheaval of the surface layers, we may safely count on an increased carbon content of the coal and a conversion of coal to a greater or smaller degree into anthracite.

Our experiments therefore justify us in saying that the formation of coal in nature takes place in two distinct reactions, namely, first the reaction of carbonization, and secondly the formation of anthracite. The former represents from the point of view of the physical chemist a reaction progressing on its own accord under ordinary pressure. The latter on other hand will not take place under ordinary pressure no matter how lone we wait. Increased pressure alone is capable of forcing the chemical system to undergo a change in the direction of increasing the percentage of carbon. In both cases elevation of temperature does not determine whether the reaction will take place or not. Rise of temperature merely hastens the reaction which goes on just as well at lower temperatures. Here there is a difference of highest significance between the effect of temperature and that of pressure. Without the latter no formation of anthracite can occur. Thus we see that it is not by no means justified to attribute to anthracite in each and every case a greater age than to ordinary coal. It is true that in many cases anthracite dates from a very early period, but ordinary coal may be just as old if not older. It remained coal because sufficient pressure was not at hand to cause the transformation.

This explains why anthracite is often found in strata which are geologically of recent date, while in paleozoic strata often coal has been found with a carbon content lower than that of coal found in mesozoic strata.

I hope to have given a short survey of the lines followed in the high pressure experiments in my laboratory. Such experiments have not merely as their aim the solution of technical problems, but lend themselves to the solution of purely scientific problems as well, for the product obtained by the artificial carboiization of cellulose lays no claim to become a substitute for natural coal and there seems little hope to

rival nature in this process with equal efficiency. At any rate today when our mines are still productive it is more profitable to rely on nature's storehouse. Perhaps in years to come, when this happy condition has ceased, the study of the process of carbonization may have more than scientific interets for the explanation of the natural process, and may serve as a basis for methods of supplying the indispensable coal. We may not be far from this point since various endeavors seem to be very promising, especially those of obtaining coal from peat by wet carbonization according to the process of Ekenberg and Testrup as worked out in this country.

Now if we ask what has enabled us to work with high pressure experiments almost as conveniently as in ordinary test tubes and flasks, the answer will lie in our ability to join tubes and bombs, with each other and with measuring apparatus without danger of leakage even at pressures as high as 400 atm. and at temperatures up to 500°. The principle of such air-tight joints first employed by Haber and Le-Rossignol rests on a union of two parts closing upon each other not with an extended surface but merely in a circular line of contact between two cone-shaped ends of the parts to be joined.

The two cones are clamped and forced together by a screw. Expansion on heating does not cause leakage because both parts expand equally especially if made of the same metal. The same method is employed for closing up the reaction vessels. We have used such cones as large as 20 centimeters in external diameter with excellent results at pressures up to 400 atm. They offer not only a very convenient means for joining and closing up tubes and bombs but they show little deterioration in use. Moreover they may be used in large number in the same apparatus without difficulty. In our own experiments we have used as many as 20 joins in one apparatus heated to 400° to 150 atm. For three weeks no decrease of pressure could be detected.

For small laboratory experiments we employ for reaction vessels hollow steel blocks. A small hole on the side gives room for a thermo-element for controlling the temperature. This is the cone which is tightened by means of a screw. The core has a tube with which valves or gas bottles may be attached to the vessel. For regulating and reducing the pressure and for closing off tubes we use the LeRossignol valve which has given complete satisfaction. With an increase in the size of the apparatus it is advisable to use large flasks of presesd steel made according to the Ehrhardt method. I have used those flasks with a capacity of twelve gallons, but they can easily be made to hold up to 200 gallons. For the general introduction of high pressure methods into chemical industry we may feel assured that no insurmountable obstacles will present themselves as far as the construction of the necessary apparatus is concerned.

THE GEOGRAPHIC DISTRIBUTION OF TANNIN PLANTS.*

By W. W. STOCKBERGER.†

The constant increase in the quantity of tanning materials which is being imported into the United States cannot fail to arouse further interest in the source of these products in the economic conditions prevailing in the countries from which they are derived. Since in recent years important additions have been made to the number of plants recognized as available sources of tannin, further knowledge regarding their abundance and general region of occurrence is naturally very desirable. Also much more definite information is needed concerning the local distribution and commercial range of all important tannin plants before either their economic significance or their practical importance as an available source of tannin for trade uses can be fully determined.

The limits of this brief and general paper will permit the mention of only a few of the salient features of the distribution of tannin plants, with very little discussion of this subject in its practical aspects, although the latter are yearly growing in importance. The significance of certain facts respecting the geographical distribution of tannin plants can perhaps be more fully appreciated if some consideration is first given to the distribution of tannin in the various natural orders and families into which plants have been grouped with respect to their relationships. This is a subject which has received very little attention except for the contribution of Dr. Dekker[1] in his invaluable monograph on the tannins, which has been freely drawn upon in the preparation of this paper. In Dr. Dekker's work the results of his own extensive researches are so combined with those recorded in the widely distributed literature of the tannins that the whole presents a mass of data from which important generalizations may be made. However, since the number of plants in which the presence or absence of tannin has been determined is relatively small in comparison with the number of known species of plants, it is very probable that these generalizations will be more or less modified by future investigations.

When the groups or subdivisions into which botanists divide the plant kingdom are considered with respect to the occurrence of tannin therein it appears that some forms of this compound appear in all of the main groups of plants, but that in every group there are many families that contain little or no tannin. In the lower groups of plants represented by the algæ, fungi and lichens, tannin is of frequent occurrence but owing to the relatively small mass of plant material furnished by these groups the total quantity of tannin produced is not sufficient to have any commercial im-

*Paper read at the American Leather Chemists Association Convention, Washington, Dec. 5, 1912.

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[1]Dekker, J., "De loolstoffen." Bulletin van het Koloniaal Museum te Haarlem, No. 35, 1906.

portance. In the next group, the mosses, very few plants have been found which give a positive reaction for tannin. The group which includes the ferns has numerous species which vary in tannin content from a mere trace to as much as 10 per cent, but it is in the higher group of seed-plants that tannin occurs most abundantly.

The subdivision of seed-plants, known as the Gymnosperms, contains a large number of plants which have a high tannin content. The most important of these are species of trees such as the pine, hemlock, spruce and fir. On the other hand among the Monocotyledons the number of families in which tannin has been found is small, and of these the Palmæ is the only one in which there are plants which furnish tannin in commercial quantity. Among the hundreds of species of the families which include the grasses, sedges and lilies, the occurrence of tannin even in very small quantities is quite rare.

The last and most important division of the seed-plants, the Dicotyledons, furnish by far the largest number of plants rich in tannin. The respective natural orders comprising the Dicotyledons vary greatly, as has been pointed out by Dr. Dekker, in respect to the manner in which tannin is distributed among the various families. In every order it frequently occurs that of two closely related families the plants of one will be rich in tannin while in the plants of the other, tannin will occur either in very small quantities or not at all. Occasionally there seems to be a gradual variation in tannin content between closely related families. Some natural orders contain no families of plants at present known to produce tannin, and in other orders almost the entire range of families furnish plants containing tannin but in very limited quantities. From the information which is at present available it does not seem possible to establish any very direct correlation between the production of tannin by different families of plants and their relationship to any of the schemes of classification which are in use by modern botanists. Since, however, most of the known facts concerning the distribution and abundance of plants have been collected and arranged with reference to the botanical classification it will be desirable to recognize the usual divisions into orders and families for the purpose of more clearly setting forth the general facts concerning the geographical distribution of plants producing tanning.

Turning now to the actual question of geographical distribution of plants producing tannin, we may at once dismiss from consideration all of those families in the previously mentioned classification other than the seed-plants. We will consider for convenience of discussion each of the three main groups of seed-plants beginning with the Gymnosperms. In this subdivision practically all of the plants known to contain tannin occur in one of four natural orders, the chief of which is the Pinaceæ, to which belong the pines, spruces, hemlocks and firs. The distribution of this group in the northern hemisphere naturally follows closely that of the coniferous forests and aside from the occurrence of a species of Podocarpus, in Southern Africa, and a species of Phyllocladus in Tasmania and New Zealand, there are no important taninn-bearing representatives of the Gymnospers to be found south of the Equator. The distribution in the Northern Hemisphere coincides in a more or less general way with the principal mountain ranges, the slopes of which are naturally wooded with forests of coniferous trees. This of course tells nothing of the distribution in detail but merely indicates the densest areas on which plants of this group, having a high tannin content, may be found. Scattered generally throughout certain sections of the United States and Mexico, as well as through regions in Central and Northern Europe and Asia, are many tannin-bearing species which belong to this group, but since by far the largest number of important species are included among either the pines, hemlocks or spruces, it follows that the general distribution of this group of tannin plants conforms quite closely to that of these species of trees. So far as known it appears that the tannin-bearing Gymnosperms are practically confined to the north temperate zone, and because of their accessibility and the inroads made upon them in order to meet the increasing demands for timber it is probable that this source of tannin will be one of the first to be exhausted.

The second group of seed-plants, the Monocotyledons, is quite unimportant from the standpoint of tannin, although it contains many hundreds of species of plants which are well known and widely distributed. Here, as was stated, belong the grasses, of which there are more than 3,500 varieties, but only four or five of these are known to contain tannin. In the one order which contains all of the tannin plants of importance, two only are worthy of mention here. These are the palmetto of Florida and Areca Catechu of India, which is one of the commercial sources of cutch. There are 35 other orders in this group, the plants of which are widely distributed, but they are so poor in tannin that from the commercial standpoint at least they cannot be regarded strictly as tannin plants.

The third group of seed-plants, the Dicotyledons, contains by far the greater number of tannin plants. In some of the natural orders of this division tannin producing families are practically wanting, in some the relative number of tannin families is variable, and in others practically every family contains tannin producing plants. A study of those natural orders in which only a part of the families contain plants rich in tannin reveals some interesting facts. Several of these orders are widely distributed both with respect to climatic conditions and continental location. Representative species which contain tannin occur in various situations ranging from the tropics to areas approaching the limits of vegetation toward the poles. How-

ever, when the locality is considered, of such plants as have been found to yield tannin in percentages sufficient to make them commercially promising, it becomes evident that with few exceptions they are all to be found in tropical countries. This fact may be concretely illustrated by citing the distribution of some of the more important tannin plants belonging to those natural orders in which there is great variation between families with respect to tannin production. For example, the natural order Urticales has three tannin producing families comprising about sixty species of plants of which those highest in tannin, 4 to 14 per cent, are a few species of Ficus growing in India and the Philippines. In the order Santalales four families together contain about fifteen species of plants which produce tannin, the important ones being species of Osyris and Fusanus from India, Central Africa and Australia, ranging from 15 to 25 per cent in tannin content. The order Ranales has nine families which together include a hundred species of plants containing more or less tannin; of these the best known are species of Persea in Chili, 17 per cent tannin; Nectandra in Brazil, 10 per cent tannin; Nesodaphne in Australia and Litsea in India, both yielding over 7 per cent tannin. In the order Tubifloræ a large number of tannin containing species is distributed among fourteen families. The important tannin plants are species of Bignonia from Guiana, 14 per cent tannin, of Eremophila from Australia and of Avicennia from the East and the West Indies. Other orders in which a part of the families have numerous species containing tannin, the important ones of which are largely confined to the tropics, are the Contortæ, Aristolochiales, Rubiales, Umbelliflora, Parietales and Malvales.

No less interesting is the distribution of those orders in which practically all the families comprise tannin bearing plants. In some of these families the occurrence of tannin is so general that they may be considered as typical tannin families. Examples of such are the Combretaceæ, consisting of about 240 tropical species, one of which yields the myrobalans of commerce; the Rhizophoraceæ which contains about 50 tropical species rich in tannin, some of which yield the mangrove bark; the Leguminosæ with about 6,000 widely distributed species of which many of those rich in tannin, as the wattle, algarobilla, ratanhia, kino and divi-divi, are tropical, and the Myrtaceæ which has at least 100 tannin species, the best known of which is the Eucalyptus, native of Australia. Notwithstanding the wide distribution of these families, by far the greater number of species having a high tannin content occur in tropical or subtropical regions. There are, of course, some exceptions, as, for example, the Fagaceæ, to which the oaks and chestnuts belong, but in general that portion of the several continents lying between the parallels of 30° north and south latitude must be depended upon to furnish the bulk of the supply of commercial tannin.

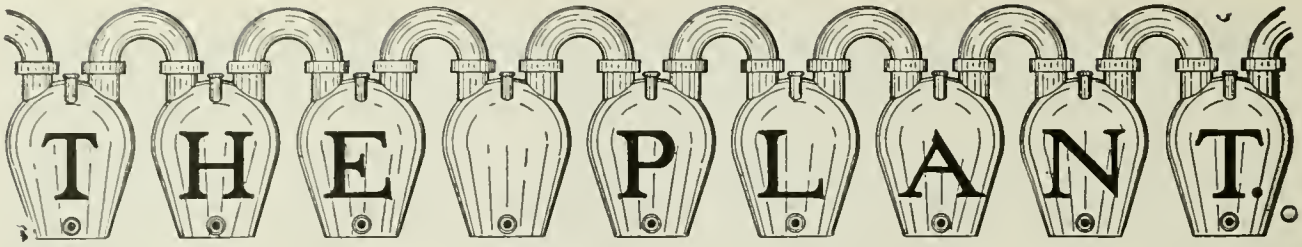
An enumeration of the various plants which have been used for tanning in different countries would give only an apparent indication of their geographic distribution, since a tannin plant frequently occurs in countries where it finds little if any use and perhaps more frequently its greatest use is in countries where it does not naturally occur. In many cases it is equally unsafe to judge of the botanical distribution of these plants from the localities given as the source of the material used in the analyses reported in the literature of the tannins. The writer recently examined what purported to be a list of the most important tannin plants of the world in which the country where each species occurred was given. On tabulating this list the following distribution of the species was obtained:

India	68 species	Chili	3 species
Europe	40 species	Brazil	3 species
Australia	22 species	Argentine	3 species
North America	16 species	New Zealand	3 species
Africa	9 species	Peru	2 species
Central America	7 species	Guiana	2 species
China	3 species	Asia	2 species
Japan	3 species	Mexico	1 specie

A number of reasons might be given for the apparent inequality in distribution shown by the compilation, but it will suffice to say that botanical exploration, particularly with respect to economic plants, has been carried much further in India and Australia than in other tropical countries, and that when these countries shall have been fully explored substantial additions will probably be made to their lists of tannin plants. In this connection mention may be made of a note by the writer in the Journal of this association in which attention is called to thirty-five species of tannin plants in Paraguay, only one of which is referred to Paraguay in most of the literature on tannins.

The present state of knowledge with respect to the distribution of tannin plants leaves much to be desired. The lack of information is not confined to the conditions in the less accessible tropical countries alone, but is evident also wherever it becomes desirable to secure full details concerning the production, handling and utilization of any tannin plant. In the judgment of the writer there is less need for concern regarding the possible exhaustion of the natural supply of tanning materials than for a practical solution of the problem of how to bring them into the market on terms that do not work a hardship either to producer or to consumer. So long as these materials can be obtained from untilled or untillable areas of land with the assistance of low priced labor their production as an agricultural crop will porbably be very limited. But should economic conditions so change as to enable certain tannin plants to compete successfully with general field crops there is no doubt that large quantities of tanning materials could then be produced on an agricultural basis.

[1] Stockberger, W. W., Tannin Plants of Paraguay, Journal of the American Leather Chemists Association, April, 1912, p. 185-192.



CHEMICAL CONTROL IN MANUFACTURE OF MIXED FERTILIZERS.*

By J. S. BROGDON.†

The importance of chemical control in the fertilizer factory becomes very apparent to the commercial chemist, who, by reason of hundreds of chemical analyses of the products, becomes familiar with the regular manufacturing practice of many factories. In very few instances are the mixed fertilizers found to analyze below the guaranteed analysis, but in practically every factory that has favored the writer with patronage during the past five years the amount of value in overages has been excessive, and in many cases the losses have been appalling. The necessity of a liberal amount of margins is recognized, but experience has demonstrated the feasibility of deciding what the margin should be and then controlling the mixing of the fertilizer to conform to that standard.

The average has been made of all analyses made in this laboratory of complete fertilizer during the past two years for firms not using chemical control. In cases where the analysis was below guarantee, proper correction was made in the average. The figures given in Table I show the losses of a great number of firms, and the results, no doubt, represent the general practice of the firms represented, for such a number of analyses will average the several errors of sampling and mixing. Below this average is given the margins the writer has found possible to maintain during the past two years in plants operating under strict chemical control, and last is shown the loss resulting from the lack of chemical control.

TABLE I.—SHOWING LOSSES DUE TO LACK OF CHEMICAL CONTROL.

	Available	Ammonia	Potash
	Per ct.	Per ct.	Per ct.
Average of all overages for two years without chemical control	.57	.24	.47
Margins with chemical control...	.15	.05	.15
Losses due to lack of chemical control	.42	.19	.32

Considering acid phosphate to be worth 50 cents per unit, ammonia to be worth $3.00 per unit, and potash to be worth $1.00 per unit, the losses in dollars and cents amount to $1.10 per ton. Such stupendous losses are not made by all these firms because of some fault in design of plant or machinery, nor is it reasonable to believe that they are due to any peculiar system of management of any one plant, for the average represents many factories with many managers and superintendents. The reason, then, must lie in some common error or errors. The writer has given this matter careful investigation and, as an unbiased onlooker, with the data in hand, has come to the conclusion that the losses must be charged about equally to the doors of general managers and superintendents. These officials seem to have made in general the same error.

The full value of chemical control has not been recognized. Very few managers or superintendents have had theoretical training. As a result the fine points of chemistry, not being fully understood, have been ignored. Since the fine points of chemistry have not been stressed by the managers, it is a natural thing that they have not received the special attention of the factory superintendents. In one instance during the past season, in billing, an error was made in the initials of a customer. The writer is aware that four letters were written the superintendent on this matter, while several certificates of analysis in which the ammonia was found to be running high were ignored. As a result the superintendent, who is, of course, desirous of pleasing the manager, gave much attention to the details of billing, and allowed the mixing of fertilizer to go its own course. At the end of the season the overages on over a hundred analyses of complete fertilizers was averaged.

The writer wishes to explain at this point that these analyses were not made in this laboratory. It was found that the losses had run up to over $10,000 when computed on the average of the analyses. The average of the analyses was then totally disregarded, and the losses computed on the basis of the stock report. By this system the losses were reduced considerably. It must be remembered that a stock report is an estimate; such a thing as accurate stock taking in a fertilizer factory is a most difficult matter. The writer does not believe it is of much value to make chemical analyses if the samples are taken in a crude way and if "quick lunch" laboratories are patronized, for such procedure is recognized as not having any value when it comes to the loss and gain account at the end of the season. Further, if such data had been properly understood and corrections made at the time, the losses would not have occurred. The packers and large fertilizer interests have long since recognized the importance of chemical control, and have delegated this responsibility to a chemist.

Some independent plants maintain a laboratory and employ a man to make chemical analyses, preferring

*From The American Fertilizer.
†Analytical Chemist, Atlanta, Ga.

that he occupy his time in this way. It is not unusual for the chemist to be told to "stick to his laboratory and not go prowling about the works." The really important thing is to bring together the problem and the man competent to solve it. The analyses will only illuminate the problem—not solve it. The usefulness of the chemist in a plan to a large extent is determined by the importance which the manager places upon the services of the chemist and the importance which he expects the superintendent to attach to the fine points of chemistry. It has been said that the enemy of waste is efficiency—efficiency is promoted by system. Any system is of little value if it is not carried out every day. For success the system must be simple and not require any great amount of learning or expenditure of energy, for laborers cannot be expected to look after any great amount of detail. For success the system must be automatic.

First of all is the systematic analysis of all materials as they are received, and the certificate of analysis should bear the storage position of these materials, and the walls of the storage shed should be marked with chalk, showing the analysis. In making these analyses, particularly with tankage, it is not sufficient to give the bone phosphate of lime analysis, but the available phosphoric acid must also be shown. The available can only be found by analysis. As far as it is possible the materials of the same grade should be stored together; that is, if two cargoes of potash are to be received in one season, one cargo should be stored on one side of the house, and the second cargo on the opposite side.

In this manner the mixing of complete fertilizer is greatly simplified by using the same grade of potash on a given machine all through the season. After the materials have been analyzed a basis formula book must be made in duplicate. In this book a formula should be calculated for each and every brand on a basis of the analysis of the materials in stock. It will be found necessary to vary these formulæ from time to time with variation of the material. The overages should be plainly shown on each brand, and the percentage available, the percentage of ammonia and the percentage of potash as derived from each ingredient should be shown.

FORMULA FOR 10-2-2 FROM TANKAGE AND SULPHATE AMMONIA.

	Avail. Per ct.	Amm. Per ct.	Potash Per ct.
1,060 lbs. 18.25% Acid Phosphate....	9.62	..	..
260 lbs. 9% and 4% Tankage.....	.54	1.17	.05
70 lbs. 25% Sulphate Ammonia ...	..	.87	..
195 lbs. 21.50% Manure Salt	..	..	2.09
415 lbs. Ground Limestone	..	..	..
2,000 lbs.	10.16	2.04	2.14

The systematic inspection of all weighing and measuring devices is of paramount importance. It will be found to be very economical to have an intelligent, well-paid man at each pair of scales. There is no greater source of error in a fertilizer factory than the banking of materials under the platform of the scale, which will impair the accuracy of the scale to an untold extent. The platform and the frame of the scale must be swept frequently. The writer has not found the plan of letting the man who pushes the cart balance the scale, to be in any measure satisfactory. Many errors are due to this one cause.

In some few factories, scales are not used, but measuring boxes are preferred. It will be found expedient in such cases, as where there are two grades of cottonseed meal, to paint the boxes different colors, the red being for the 7½ per cent meal, and the green for the 8 per cent meal. Red tags and green tags should be tacked on the wall opposite the meal of corresponding grade. This general scheme will be found helpful throughout the factory for tankage, etc. The laborers can be told to use red meal or blue tankage, etc.

It is possible to produce as thorough mechanical mixtures using the old-style continuous-mixing machine as can be obtained with batch mixers. As a general rule, however, better results can be obtained from the latter machines. One of the main difficulties with the old-style mixers is the matter of segregation when the machine is not running at full capacity. If a single barrow holding the ingredients for one bag is dumped into a contiuous mixer, and the sack filled from the hopper, a large portion of the ammoniates will be in the bottom of the bag, and a large portion of acid phosphate will be in the top of the bag. For successful operation the continuous mixer must be operated at full capacity all the time.

The importance of good mechanical condition in acid phosphate and other materials cannot be overestimated. Materials which are inclined to be lumpy should be passed through a screen, for otherwise the analysis of the mixed goods will be found to be very erratic, even though the proper weight has been introduced.

In calculating the available phosphoric acid, due consideration must be taken of the fact that acid phosphate will dry out in passing through the machine. An acid phosphate which analyzes 17½ per cent in the pile can safely be considered to be 18 per cent, due to this drying out. This, perhaps in a measure, explains the great tendency of mixed goods to run high in available.

PHOSPHORIC ACID.

The importance of systematic daily analyses of the mixed goods cannot be overestimated in the matter of chemical control. It is a very grave error to make composite samples of a week's run as a basis of chemical control. It is logical and expedient that each day's run and the run from each machine should stand for itself. While it is not at all practical to analyze every brand from every machine each day, it will be found advantageous and profitable to analyze one sample from each machine every day. This places responsibility and stimulates interest. A very good scheme for taking these samples is to tack fertilizer bags on the side of the wall at each machine, one bag for each brand. During the day, as each brand is made, a sample should be taken and placed in the proper bag. At the end of the day the superintendent can select at

random a brand for analysis. The sample should be screened and quartered and the date and machine number attached before sending to the chemist. (See "Sampling of Fertilizers," American Fertilizer Hand Book 1913). This scheme will encourage the foreman to maintain his highest efficiency at all times. At the end of the season the average of the overages obtained in this way must be of great importance in establishing factory practice. Not only can the work of the entire factory be known, but the work of each foreman.

SCHOENHERR AND BERKELAND-EYDE ELECTRIC NITRATE FURNACES.

By FRANK C. PERKINS.

The accompanying illustrations and drawing show the electric furnaces of the Schoenherr and Birkeland-Eyde type for producing nitrates by the oxidation of atmospheric nitrogen and the hydro-electric plants in Norway, supplying the current for operating these nitrate electric furnaces.

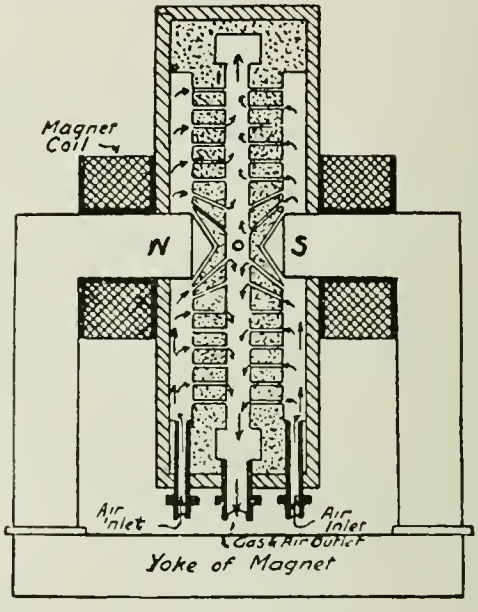
In explaining the Birkeland-Eyde method, Dr. Samuel Eyde states that it is necessary first to describe the electric flames consisting of arcs of light which are used in the electric furnaces. It is pointed out that the formation of the flame occurs by an arc of the electric flame being formed between the points of the electrodes, which are close to each other. By this means in a highly magnetic field. The electric arc that has been formed moves on account of this magnetic field with great velocity perpendicularly to the lines of force, and the electric arc's foot draws back from the points of the eltctrode. As soon as the length of the electric arc increases the electric resistance becomes greater and the tension increases, until it becomes so great that the new electric arc starts from the points of the electrodes.

In order to regulate the current an inductive resistance is used in series with the flame. With alternating current all the arcs are formed alternating in opposite directions and appear to the eye to be circular discs. This flame provides a powerful technical means for the oxidation of the nitrogen of the air. The flame in the furnaces burns with a steadiness that is really astonishing. It may be stated that the electrodes are thick copper tubing, through which water passes for cooling purposes. The chamber in which the flame burns is circular, of only a few centimeters in width, and about three meters in diameter. The electric furnaces are lined with fire clay brick, through the walls of which the air is admitted to the flame. The nitrous gases formed in the flame escape through a channel made along the casing of the furnace, which like the flame chamber is furnished with fireproof bricks.

To supply the furnace with the amount of power desired, each one is furnished with an induction coil, by means of which the power is regulated as required. The induction coil serves, moreover, to keep the flame in the furnace steady and even while working.

It is held that with this furnace there was obtained such steady working that it burns for weeks without any regulation worth mentioning. The maintenance of the furnace and its repair are simple as the most exposed portions, the electrodes, need be changed every third or fourth week, and then only a small part of them. The fireproof masonry is changed every fourth to sixth month.

The temperatures in the flames exceed 3,000° C. The temperature of the escaping gases may vary between 800 and 1,000°. The furnaces are made of cast steel and iron, the middle of the furnace being in the form of a circular flame chamber. The electrodes are



Section of Birkeland-Eyde Furnace.

led radially into this flame chamber. By aid of centrifufal fans the air is brought into each furnace through tubes from the basement.

Furnaces have been built which consumed energy from few horse power up to 5,000 h.p. Later Dr. Schoenherr, with the electrical engineer Hessberger, of the Badische Co., perfected an electric furnace for the oxidation of atmospheric nitrogen constructed on quite different principles. In place of the great disc of electric flame, he developed a long slender arc in the axis of a narrow iron tube through which a current of air is forced.

It is pointed out that the Schoenherr furnaces now used consists of a slender vertical column of iron plates 7 meters in height. The inner tube is the reaction chamber, the others form channels for the entrance of the air current and its exit after coming in contact with the flame. In this way the heat of the outgoing gas is transferred to the ingoing current. The main electrode is at the lower end, and is moveable in a vertical direction, as it must be raised from time to

time when the end is worn by the arc. The reaction tube serves as the second electrode. By means of a lever the space between the electrode and tube can be bridged over and the arc formed.

It is said that the air current forced by a powerful aspirator enters in the lower part of the furnace and passes the channels. The entry into the reaction chamber is through a number of small tangential openings arranged in several horizontal rows in the sides. The current passes in this way around the chamber and the arc is driven up in the midst of the rapidly moving current of air. As a rapid cooling is of importance in securing a good yield the upper third of the tube has a water jacket through which the gases pass, and in this way the reverse reaction is prevented to a notable degree.

It is claimed that the reaction is identical with that obtained in the Birkeland-Eyde furnace and the yield is practically the same amount of nitrate per horsepower used.

In these electric nitrate furnaces the air is procured by swiftly revolving ventilators and is conducted through large iron pipe lines to the furnaces. These are at Notodden, only furnaces of the Birkeland-Eyde system from 1,000 to 3,000 kw. capacity while at Rjukan furnaces of the Birkeland-Eyde system of 3,000 kw. are used, as well as furnaces of the Schoenherr system, all of 1,000 kw.

As soon as the air in the flame chamber has been acted upon by the electric flame the nitrous gases formed pass out through pipes, which convey the gas to the steam boilers in which the temperature, which was 1,000° C. is reduced. The steam produced in the boilers is utilized in the further treatment of the products. In the boiler house there are also air compressors, which supply compressed air for pumping acid and lye in the various chemical departments. It may be that the gases pass on from the steam boilers through an iron pipe into the cooling house, and complete the cooling begun in the steam boilers. Each cooler consists of a great number of aluminum tubes, over which cold water runs while the hot gases pass through them. The temperature of the gas is considerably reduced. From the cooling chambers the gases pass to the oxidation tanks. It is pointed out that these oxidation tanks are vertical iron cylinders, lined with acid proof stone. The object is to give the cooled gases sufficient period of repose, in which time the oxidation of the nitrogen oxide may occur. The necessary amount of oxygen is present in ample quantity in the air which accompanies the gases from the furnaces. From the oxidation tanks the gases by blast engines are led into the absorption towers. The towers are filled with broken quartz, which is neither affected by nitrous gases nor by nitric acid and the assist the passage of the gases on their way from the furnaces there are centrifugal aluminum fans on each row of towers. The gases enter at the base of the first tower, go up through the quartz packing and thence by a large earthenware pipe enter the top of another tower, through which they pass downward through the quartz to the bottom of the third tower, and so on, until the air relieved of all nitrous gases leaves the last tower.

Water is allowed to trickle through the granite towers and this is gradually converted into a weak nitric acid, while the liquid used in the iron towers is a solution of soda. The absorbing liquid enters the top of the tower and is distributed in jots by a series of earthenware pipes, so that the permeating gases enter into immediate contact with the absorbing liquid. Nitric acid is thus formed in the granite towers and in the iron towers a solution of nitrite of soda.

There is a constant even stream running into the granite cistern from the bottom of the towers. It flows into the montejus which serve to pump up the acid, which has to pass repeatedly through the tower before it has become strong enough for the purpose for which it is intended. These montejus are worked by compressed air and send the acid up into large stone arc tanks. From these jars the acid again runs through the towers. The montejus working automatically. The iron towers percolating through a solution of soda, owing to its far greater power of absorption, affects the separation of the last remaining traces of nitrogenous gases from the accompanying air. Of the entire quantity of nitrous gases passed through the absorption system, about 97 per cent is absorbed. It is of interest to note that the finished nitric acid coming from the towers, which has a strength of about 30 per cent by volume, is collected in granite cisterns from which it is drawn to what is called the dissolution works. These consist of granite vats filled with limestone, over which the acid is poured. This drives off with violent effervescence, the carbonic acid of the limestone. The nitric acid takes its place and forms a watery solution of nitrate of lime or calcium nitrate. The rest of the acid is neutralized in a small tower filled with milk of lime and is now jumped into vacuum evaporating apparatus. A great saving in heat is effected by boiling in vacuum. The steam required for the evaporation is obtained from the steam boilers, heated as before mentioned, by the furnace gases. The concentration of the nitrate solution in the evaporizing plant is continued until the specific weight of the liquid at an even temperature shows a content of 13 per cent nitrogen.

It may be stated that this solution is then sufficiently evaporated, and can be pumped up into the solidification chambers, where it is conducted upon a revolving cylinder, cooled on the inside. It stiffens so rapidly that it will easily spring off into small leaf-like pieces, which can be granulated without difficulty in the crushing mill. There the mass is reduced to a granular state. Finally the coarse powder produced is raised by an elevator to a vat, from the bottom of which it is dumped into casks holding 100 kilos net

weight. The gas lead into the iron tower forms with the solution of caustic soda a solution of nearly pure sodium nitrite. This is concentrated by evaporation in the same sort of apparatus as above and allowed to crystallize. The crystals are dried in a centrifuge and put up in barrels which are lined with paper to guard against dampness.

Besides these two products nitrate of lime and ni-

View of Rjukan Power Station.

trite of soda, the Notodden works have taken up the manufacture of concentrated nitric acid and nitrate of ammonia, which are largely shipped to America from the Norway plants.

It is pointed out that for the development of the atmospheric nitrogen industry the question of water power is most important as this industry cannot exist unless it can procure cheap water power. There is no country in the entire world that can boast of more favorable conditions in this respect than Norway and the enormous rise of this industry must be attributed to a very large extent to Norway's great opportunities in the amount of hydro-electric power available. It may be stated that Norway has not only her magnificent and high waterfalls but that she has large mountain lakes, permitting the construction of enormous natural reservoirs for conveying the water to the power station. The nitrate works now are all situated in the southeastern part of Norway, in the Telemark river district.

Among the most important nitrate works are Notodden factories situated on the lake of Hiterdal, about 50 ft. above the level. A short channel with a series of locks permits communication with the town of Skien, an important seaport at the head of the fjord. It is said at present vessels of 200 tons can ascend to Notodden and it is planned to enlarge the locks so as to allow the passage of seagoing vessels of 2,000 tons. The ability to ship directly to all parts of the world by water with one trans-shipment is an important factor in the future of the manufacturing of Notodden nitrate. The Notodden factories which now use about 60,000 h.p. secured from two neighboring water falls, at Lienfos and Svaelgfos.

It is of interest to note that at Lienfos, about two miles from Notodden there is a dam with a fall of about 55 feet. The volume of water being 75 cubic meters per second. The power station is equipped with four units of 5,000 h.p. each, making a total of 20,000 h.p.

There is also the larger Svaelfos power house situated above and about one mile from Lienfos where volume of water is the same as at Lienfos. The dam has, however, a fall of about 165 ft. A tunnel takes the water to the reservoir, from which four flumes out into the solid rock conduct the water to the station, where there are four sets of turbine generators of 10,000 h.p. each. The generators are capable of producing 13,000 h.p. and are among the largest units in the world.

The power from these two waterfalls is transmitted to Notodden by six separate transmission lines, each line consisting of six cables, 12 millimeters in diameter. The three phase alternating current of 50 periods is transmitted with a voltage of 10,000. A second power station at Svaelgfos is now under construction. As the normal volume of water by an additional regulation of distant lakes in the same watershed increased to 90,000,000 cbm., in the new power station two units of each 10,000 h.p. will be built.

There was built about 16 miles further up the river the first regulating dam at the lake of Tinn at the

Lienfos Power Station.

same time as the water station of Svaelgfos and the factories at Notodden. The immense basin created by this dam makes it possible to store up fully 300,000 cubic meters of water. For transportation purposes to and from the Rjukan factories it was necessary to build two railways, one of 19 miles, from Notodden up to the lower end of the lake of Tinn, and one ten miles from the lake up to the factories at

Saaheim. Ferry boats and large barges are used for transportation on the lake between the terminals of the railways. The railroad from the lake up the narrow valley to Saaheim passes just beneath the large mountain Gausta, a few miles further up Saaheim and the factories are situated.

The electric power transmission line was built on heavy iron masts. About 2½ miles from the factory up in the valley lies the power station, a large building of granite about 120 meters long. The Rjukan waterfall lies one mile further up in the valley. It is not only this waterfall itself, but the total fall in the river of a distance of about six miles which is to be harnessed up.

Two power stations are provided for, first, at Vemork, on a ledge of the cliff, 1,000 ft. below the terminal reservoir of the tunnel. The water is conducted from the reservoir down the mountain side to the turbines in ten huge flumes, side by side. These flumes are 5 ft. in diameter. The upper sections are of riveted steel plates, the lower, where the pressure reaches 30 atmospheres, are made of welded plate, one inch in thickness. They rest upon a foundation built upon the solid granite of the mountain.

It may be stated that the water descends 971 ft. to the Vemork turbines and upon leaving the power station the water enters another tunnel, excavated in the side of the cliff, and is conveyed to a point slightly more than three miles down the valley where a similar series of flumes for the second power house. The total fall here is 909 ft. These two power stations will furnish the factories with 250,000 h.p. or 270,000 h.p. when completed.

Interior View Svelgfos Power Station.

There are in the Vemork power house ten units each of 14,000 h.p. Pelton wheels being used in the turbines on account of the great pressure of water, with a maximum capacity of 17,500 h.p. A three phase alternating current of 50 periods is transmitted from this power house to the nitrate works through 60 wires, partly of copper, but chiefly of aluminum. The working voltage is 10,000.

There is a reservoir on the top of the flumes blasted out of solid rock from the intake, where a dam is built across the river. For the regulation of the water supply a dam has been built at Lake Mosvand by means of which the level of the lake is raised over 46 feet. As the surface of the lake is not less than 23 sq. miles, nearly 900,000,000 cubic meters can be retained. It is said that the minimum flow in the river is in this way increased from 5 to 47 cubic meters per second, or the water power at Rjukan only from 30,000 to 250,000 h.p.

Birkeland-Eyde Furnaces at Rjukan.

VULCANIZED FIBER IN GERMANY.

A recent U. S. Consular Report contains the following notes on the use of vulcanizing fiber in Germany:

The demand for vulcanized fiber in Germany has about doubled within the last five years, and although the principal supplies are received from the United States, it is stated that competition from England and Sweden is more serious than formerly and prices consequently somewhat depressed. A number of American firms are well represented in Hamburg, selling their fiber to various German concerns which convert it into those articles to which it is adapted. The addresses of German concerns which use imported fiber as a raw material for further manufacture appear in a separate list (available from the Bureau of Foreign and Domestic Commerce, Washington, D. C.). It is impossible to state their individual requirements, as this is a point upon which they are indisposed to give information.

Vulcanized fiber, or to employ the German term "vulkan fiber," is dutiable in Germany at 6 marks per 100 kilos ($0.648 per 100 pounds) under tariff No.

651. The rate applies to the following articles: "Glazed boards (pressed board) and other highly finished cardboards, imitation leather board and other fine cardboards, whether dyed in pulp or not; vulkan fiber."

The amount of importations and exportations of the last few years appear in Table I:

TABLE I.

	Jan. to Aug.	Twelve Months.				
	1912.	1913.	1909.	1910.	1911.	1912.
	Tons.	Tons.	Tons.	Tons.	Tons.	Tons.
Total imports	890.7	1,227.7	689.7	834.4	1,124.3	1,012.5
From Sweden...	(1)	(1)	60.5	57.5	(1)	(1)
From Gt. Britain	39.7	92.4	(1)	(1)	76.3	62.6
From U. S.....	834.3	1,123.6	596.6	720.4	1,024.6	923.7
Total exports	38.3	57.3	33.1	62.3	86.3	92.8

(1) Not stated in official statistics.

Vulcanized fiber is not manufactured in Saxony, and there is said to be only one factory in Germany, although there is a large and growing demand for the material. The industry seems to be so highly perfected in the United States, and such ample provision is made for meeting the demands of foreign consumers, that competition on this side of the water is practically out of the question.

The material is used chiefly in connection with machinery for toothed wheels, packing, valves, collars, brakes, and a variety of similar objects. Large amounts are also required by trunk makers. As the manufacture of machinery is a prominent feature in Chemnitz, and the number of textile machines in active use in the region extends far into the thousands, the consumption of fiber has recently become of considerable local importance.

There are four firms in the city of Chemnitz that sell vulcanized fiber to machine builders, textile works, etc., but a large number of consumers purchase directly from the Hamburg jobbing agents of American fiber works. These local dealers secure their supplies from the same sources. The leading local dealer states that his annual sales amount at present to about 12,000 pounds. He would very gladly enter into direct relations with an American manufacturer rather than deal with middlemen in Hamburg. He sells considerable fiber in the form of piping and round rods, but the chief demand is for sheets. The softer variety is uniformly red. Hard fiber is supplied in black, gray, or red. The sheets are furnished in lengths varying from 160 to 180 centimeters (5.2 to 5.9 ft.), with breadths of 100 to 120 centimeters (3.3 to 3.9 ft.).

According to the trade journals, the prices of caustic potash in Great Britain remained very constant during 1912. The price May 28, 1913, for 90 per cent potassium hydrate was $103.41 per long ton, and for 75 to 80 per cent, $94.90. It is understood that these are the prices for goods delivered on the wharf at the port of arrival.

ALUMINUM CARBO - NITRIDE: EXPERIMENTAL EVIDENCE OF DISSOCIATION AT TEMPERATURES ABOVE 1450° C.*

Of the many nitrogen fixation methods proposed during the past half century, none, so far as has been made public at this time, shows fairer promise of commercial feasibility than the double nitride of aluminum and carbon, which in the absence of a definitely established structural formula is called aluminium carbo-nitride.

This compound may be expressed by the skeleton formula $Al_2C_3N_6$, and would contain, if chemically pure, 48.24 per cent nitrogen. Its chemical structure is indicated by the following chemical equation:

$$Al_2O_3 + 6C + 3N_2 = Al_2N_2.C_3N_4 + 3CO.$$

Aluminium carbo-nitride has apparently the same structural linkage as the so-called calcium cyanamid, and possibly it should be called aluminium cyanamid; but there are many reasons why the cyanogen member is of doubtful authenticity.

So far as is publicly known at this time, aluminium carbo-nitride was first made in 1911, as a resulting product of a systematic research upon various aluminium carbides, etc. A mixture of alumina and carbon was heated in the presence of nitrogen under various conditions of temperature and pressure, and the product carefully examined. The well-known Arsem furnace was used (Vol. IX, page 153, Transactions of the American Electrochemical Society), the nitrogen being produced by chemical means.

The furnace charge was necessarily small, varying from 10 to 15 grams of mixture, which was enclosed in a carbon crucible. Thus the nitrogen could reach the charge mixture only by passing through the walls of the crucible. It was observed by means of a blank run that the furnace gases rapidly circulate through the crucible chamber, entering at the bottom and passing out at the top. While in actual contact with the resistor spiral, the gases are heated rapidly to about 1500° C., and, as at this temperature—at, say, 500 mm. (Hg) pressure—nearly 16 liters are required to supply one gram of nitrogen (at a fixation efficiency of 50 per cent, which is rather high), it would seem that the conditions were not especially favorable for a high efficiency of fixation. As the free space within the crucible is, during the reaction, constantly flooded with the carbon monoxide evolved, another cause for a low carbo-nitride reaction velocity is apparent.

The carbo-nitride reaction is questioned by several German experimenters, more especially by W. Fraenkel (*Zeit. für Elektrochemie,* issue of April 15, 1913). It is also claimed—and the research is again German—that aluminium carbide does not effect the fixation of nitrogen. Therefore, in the experimental

*From the American Fertilizer.

work herein described, an effort was made to determine the nature of the nitrogen fixation reaction.

If, as claimed by Dr. Caro, aluminium carbide (Al_4C_3) does not enable the fixation of nitrogen, it

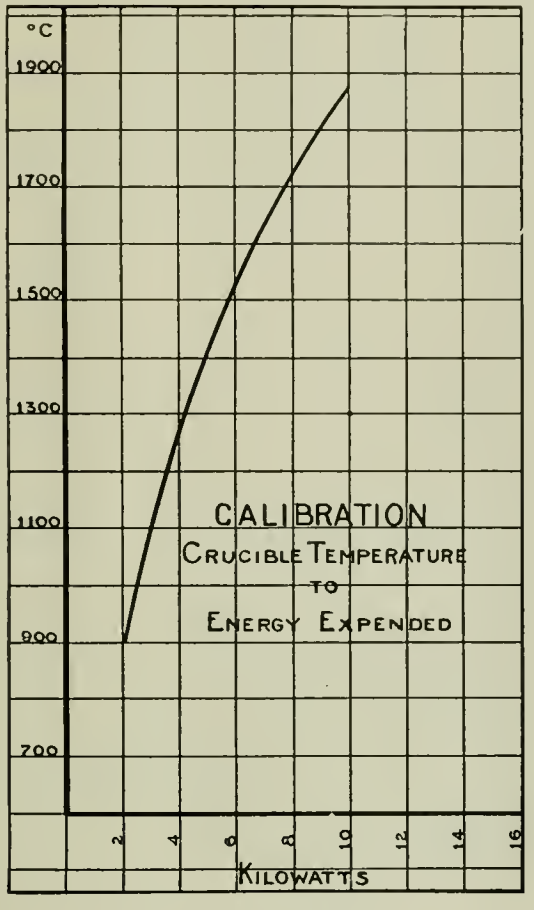


Fig. 1.

would seem that experimentation with a closed crucible, in which the carbon monoxide evolved by the carbon reaction

$$2Al_2O_3 + 9C = Al_4C_3 + 6CO$$

must pass from the crucible through its small pores, thus establishing a flow of carbon monoxide outward and opposing an inward flow of nitrogen, would impose a serious obstacle. It was assumed, in planning the experiments, that the alumina-carbon mixture first forms a higher carbide, Al_2C_3, and that this carbide reacts with nitrogen to form the carbo-nitride, and that, in the absence of nitrogen sufficient to effect such carbo-nitride reaction

$$Al_2C_3 + 3N_2 = Al_2N_2.C_3N_4,$$

the higher carbide, Al_2C_3, would dissociate to the aluminum carbide known to be stable under ordinary conditions of alumina deoxidation, viz., Al_4C_3. While the results support the assumed carbo-nitride reaction, no evidence was established showing the formation of the carbide Al_4C_3.

EXPERIMENT FACTORS.

The furnace was first operated with an empty crucible, using an atmosphere of nitrogen. Under these conditions a number of observations were made on the temperatures of the crucible (Wanner optical pyrometer) at different power loads. The results of these observations were as follows:

Kilowatts	To constant temp. minutes.	Crucible Temp. °C.
2	38	880
3	35	1,080
4	31	1,250
5	29	1,395
6	26	1,520
7	23	1,630
8	21	1,730
9	19	1,810
10	18	1,865

These data were plotted to a plain curve, as shown by the diagram, Fig. 1, giving the calibration of kilowatt variations, stated in degrees centigrade, temperature read directly upon the crucible.

From these data and a series of carefully observed pressure readings the average temperature of the gaseous contents of the furnace was established, as follows:

Crucible temp. °C.	Pressure mm. Hg.	Average gas temp. °C.
0	273	0
17	290	17
880	397	124
1,050	415	142
1,275	447	172
1,415	470	196
1,525	486	212
1,585	495	221
1,725	521	247
1,810	538	264

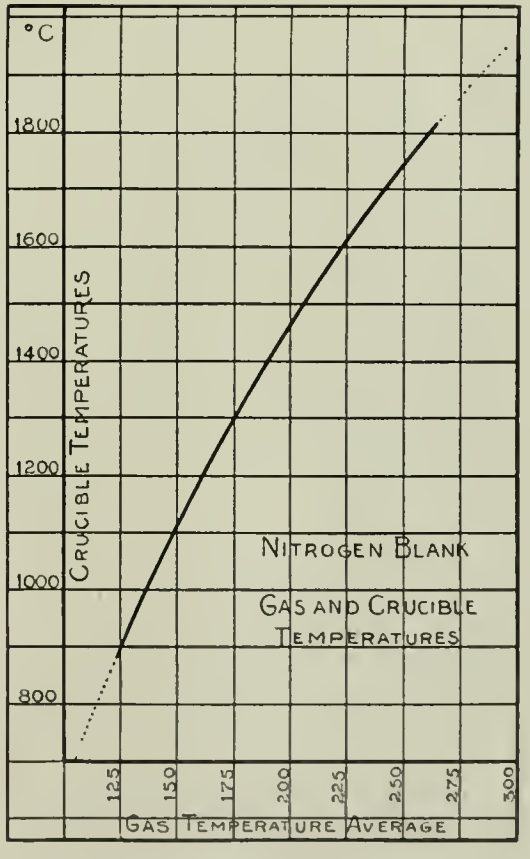


Fig. 2.

This evidence is collected in the diagram, Fig. 2, giving the record for a series of observations with the furnace containing nitrogen only and no charge. That is, no chemical reactions could have occurred within the furnace.

With these factors established it is possible to determine, while carrying on experiments, if the reactions taking place in the furnace increase or decrease the original volume of gas present. No account was taken of the possible increase or decrease of charge temperature due to chemical reactions, as, on account of the small quantity of charge and the large volume of crucible carbon and circulating gases, no material change in crucible temperature could have arisen from such cause.

Having established the temperature and volume factors, the procedure adopted was to run a charge in the furnace crucible with an ample supply of nitrogen present to convert all the aluminium in the charge to carbo-nitride.

If the nitride is formed the reaction will be as follows:

$$Al_2O_3 + 3C + N_2 = Al_2N_2 + 3CO.$$

That is, for every volume of nitrogen fixed in solid form, three volumes of carbon monoxide must be set free; hence this reaction in a closed furnace must be accompanied by a very marked increase in gas volume. If the carbo-nitride is formed, however, the reaction will be as follows:

$$Al_2O_3 + 6C + 3N_2 = Al_2C_3N_6 + 3CO.$$

That is, three volumes of nitrogen gas are converted to solid form, and simultaneously three volumes of carbon monoxide are set free. Therefore this process operated in a closed furnace would not be accompanied by any change in gas volume.

Every experiment was preceded by the removal, at least in greater part, of the gases occluded in the carbon apparatus within the furnace. This was done by heating the crucible to 800° C. and repeatedly exhausting the furnace until the manometer showed no further rise of moment. To determine the temperature at which a mixture of alumina and carbon reacts (in the absence of nitrogen or gaseous oxygen) to form carbide and evolve carbon monoxide, a run was made which demonstrated that at 1080° C. the reaction was sufficiently rapid to more than double the volume of gas present in the furnace after thirty minutes' exposure.

CARBO-NITRIDE EXPERIMENT.

The crucible was charged with a mixture containing 100 parts of alumina flour to 200 parts of ground retort carbon, both passing 40 mesh. The furnace was sealed and the crucible heated to 300° C., and the furnace repeatedly exhausted in order to thoroughly remove any moisture in the charge. The temperature was then raised to 800° C. and the furnace repeatedly exhausted to remove occluded gases. The furnace stood over night at about 3 mm. Hg, the flow of cooling water surrounding the furnace being continued all night.

The following morning the furnace was filled with pure nitrogen, at 18° C., to a pressure of 291 mm., and then sealed. Power was immediately turned on, and manometer readings taken every ten minutes. The following table gives the results noted:

Crucible °C.	Gas °C.	Pressure mm.	Normal pressure, mm.	Gain in pressure.
0	0	273	273	..
18	18	291	291	..
830	118	391	391	..
1,080	144	418	418	..
1,520	212	521	485	5%
1,595	226	589	499	18%
1,820	263	735	536	37%

The "normal pressure" gives the pressure the furnace would have shown at the average temperature of its contained gases had no gases been evolved as a

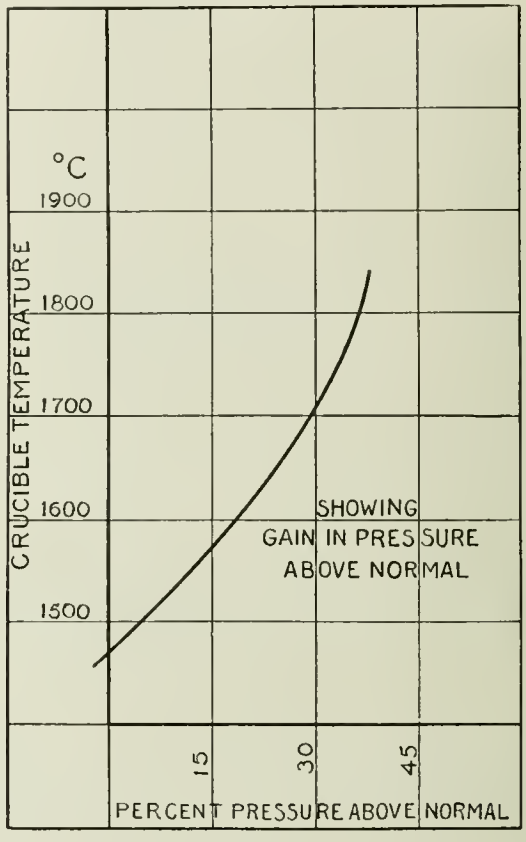


Fig. 3.

reaction product. The "gain in pressure" column shows the gain in gas volume due solely to evolution of gases in process.

The evidence is conclusive that at 1520° C. the reactions within the crucible resulted in increasing the total gas volume within the furnace, and that at 1080° C. no such reaction is apparent, though at 1080° C. and in the absence of nitrogen the charge reacts freely, with the evolution of a gaseous product.

It is assumed that at 1080° C. the carbo-nitride reaction is in active operation, and that the fact that no gain in gas volume is shown implies such reaction, and that at 1520° C. this carbo-nitride formed is suffering dissociation practically in accord with the following equation:

$$Al_2C_3N_6 = Al_2N_2 + 3C + 3N_2.$$

The assumption is supported also by the fact that in a number of the experiments the percentage by volume of carbon monoxide in the furnace gases was less at 1820° C. than at 1520° C.

The diagram, Fig. 3, shows graphically the gain in gas contents, and indicates that dissociation of carbo-nitride is markedly checked by the increasing proportion of nitrogen in the furnace atmosphere due to the dissociation.

THE FURNACE PRODUCT.

The furnace was cooled over night and the charge removed practically at room temperature. The product contained:

	Per cent.
Aluminium	23.23
Carbon	61.90
Nitrogen	10.99
Insoluble	.62
Oxygen	3.26
	100.00

The oxygen is taken by difference. The original charge contained:

	Per cent.
Aluminium	18.42
Carbon	64.76
Insoluble	.49
Oxygen	16.33
	100.00

The oxygen is by difference, and, as the materials were carefully analyzed, this determination by difference is not subject to intelligent question.

Assuming that all the oxygen in the furnace product is present as alumina, and proportioning the remaining aluminium to nitride and carbo-nitride in accordance with the known carbon content of the product, gives the following table. No carbide was found in the product. The table shows grams per hundred for comparison convenience:

	Total grams.	Al grams.	O grams.	C grams.	N grams.	Insol. grams.
Al_2O_3	6.94	3.68	3.26	....	....	....
Al_2N_2	28.38	18.70	....	....	9.68	....
$Al_2C_3N_6$	2.72	.85	....	.56	1.31	....
Free C	61.34	....	....	61.34	....	....
Insoluble	.62	....	....	....	....	.62
	100.00	23.23	3.26	61.90	10.99	.62
Charge	126.09	23.23	20.59	81.66	....	.62
Difference	26.09	....	17.33	19.76	10.99	....

It is evident at once that 126.09 grams of charge were necessary to make 100 grams of product, and that the losses in process were:

Oxygen, 17.33 grams

Carbon, 19.76 grams.

Had the process reactions consisted wholly of the following:

(1) $Al_2O_3 + 3C + N_2 = Al_2N_2 + 3CO$

(2) $Al_2O_3 + 6C + 3N_2 = Al_2C_3N_6 + 3CO$

the total reaction losses must have been carbon monoxide, in which case the losses must have been in the proportion of 0.42857 parts of carbon to 0.57143 parts of oxygen. As a matter of fact, and the Arsem furnace gives such perfect control that the results cannot be authoritatively questioned, more carbon was lost than oxygen.

In conducting the carbo-nitride experiments it was repeatedly noticed that at temperatures above 1500° C, the sight upon the top of the crucible was obscured by a dark-colored fog, and for this reason the crucible temperature was calibrated to various kilowatts upon an empty crucible. This fog was swept out of the crucible chamber by the circulating gases, and was deposited upon the water-cooled surfaces of the furnace cylinder, and was plainly in evidence upon such surfaces. As at the highest temperature obtained during the experiments the carbon of the charge could not have been vaporized, and as the individual particles of carbon as contained in the charge were too large to be carried by physical means through the crucible walls and cover, the carbon which escaped as the fog effect noted must have been derived from dissociation of a carbon compound, such as is indicated by the following reaction:

$$Al_2C_3N_6 + \text{heat} = Al_2N_2 + C_3 + 3N_2.$$

This view is also supported by the fact that no increase in gas volume was noted until the crucible temperature exceeded 1500° C., though a mixture of alumina and carbon reacts far below that temperature, and upon such reaction should have shown a marked increase in gas volume. As the carbo-nitride reaction explains why no such increase in gas volume may occur, in the absence of more conclusive data it is assumed that carbo-nitride only was formed up to a temperature of approximately 1500° C., and that above that temperature its dissociation commenced. The evidence indicates that at 1500° C. the composition of the furnace product was as follows:

	Total grams.	Al grams.	O grams.	C grams.	N grams.	Insol. grams.
Al_2O_3	6.94	3.68	3.26	....	....	....
$Al_2C_3N_6$	62.85	19.55	....	13.01	30.29	....
Free C	55.64	....	....	55.64	....	....
Insoluble	.62	....	....	....	....	.62
	126.05	23.23	3.26	68.65	30.29	.62
Charge	126.09	23.23	20.58	81.66	....	.62
Difference	....	....	17.32	13.01	30.29	....
Loss as CO	....	....	17.32	12.99	....	....

The experiments were undertaken as preliminary to a purely technical research, which, however, has not up to this time been carried out. In view of the importance of the subject, it is to be regretted that the exact quantity of carbon monoxide formed in process was not determined, and one or more experiments made at temperatures not exceeding 1500° C.

The legation of the Netherlands at Washington has extended an official invitation to the United States and the Philippines to take part in the International Rubber Congress and exhibition, to be held at Batavia, Java, from Sept. 8 to Oct. 10, 1914. Copies of the official program may be obtained from the Bureau of Foreign and Domestic Commerce, Washington, D. C.

METALLURGY.

SIMULTANEOUS DETERMINATION OF COPPER AND LEAD, WITH THE ROTATING ANODE.*

By ARTHUR J. WHITE.

In electrolyzing nitric acid solutions of copper it has been observed that lead tends to hold up some of the copper. More nitric acid is necessary for lead than will permit of copper coming down completely.

Stansbie has shown (Procedings of Faraday Soc., Nov. 26, 1912) that rotation causes copper to be comparatively insoluble in nitric acid, and he recommends continuing rotation while washing out. He claims that sulphuric acid assists in the depositition, probably because of the formation of a nitrosyl acid instead of nitrous acid, which is the active agent for copper. However, this relative insolubility may be assigned to the formation of amonium sulphate, no ammonium salt being formed in the absence of sulphuric acid. According to Easton (J. Amer. Chem. Soc., 25, 1042), nitric acid is quantitatively converted to ammonium sulphate in the presence of an excess of copper sulphate by the current.

The question arose as to whether sulphuric acid would allow of copper being completely precipitated from a nitric acid solution while lead is being determined simultaneously on the anode. It was found that it would, provided that the proportion of lead is not high enough to precipitate lead sulphate. This salt does not appear unless the proportions of lead to copper is greater than one to four, as the copper nitrate exerts a solvent action on smaller quantities.

When less than 0.15 gram of lead is present with 0.60 gram of copper, they are quantitatively precipitated in thirty minutes by a current of 8 amperes at 6 volts.

The best proportions of acid are 4 cc. concentrated nitric acid and 10 drops of concentrated sulphuric acid in a volume of 70 to 80 cc. The anode is rotated at from 400 to 700 R.P.M., and the copper is deposited on a 60-gram platinum dish at $N.D._{100}$.

THE ANODE.

The anode is of a simple form, being a small dish (3.8 cm. diameter) of platinum mounted on the end of a platinum rod 10 cm. long and 0.15 cm. diameter. The entire weight is below 15 grams, and the surface 20 sq. cm.

The surface must be roughened. This is best effected by platinizing from a 5 per cent sulphuric acid solution. Several drops of platinum solution corresponding to 0.05 gram metal were used. A current of 0.7 amp. at 1.5 volts for 30 minutes while rotating gave a dense black deposit. On ignition this turned white, and showed no tendency to loosen on continued use.

A larger, more complicated dish anode has been used before in the determination of copper (Languess J. Am. Chem. Soc., 29, 459). However, lead was not deposited upon this anode, the surface being smooth.

The ability of the rotating dish anode to hold the lead dioxide was tested.

A solution of lead was prepared containing 0.4990 gram of the pure metal. This was placed in a 30-gram platinum dish at a volume of 40 cc., 5 cc. of free nitric acid being present. The anode was rotated at 1,000 R.P.M., which was higher than was ever allowed for practical work. To the cold solution a current of 8 amperes at 6 volts was applied for 25 minutes. No tendency to splash was noticed on the cover glasses, although the temperature rose to the boiling point. A higher current could not be applied without causing the liquid to boil. After 20 minutes the dish was washed out with 500 cc. distilled water, the rotation being continued throughout. The current dropped to zero, the dish was removed, and, after the water was shaken well from the lead by a minute's rotation, the anode was dried for 15 minutes at a temperature of 130° C. The anodes were always dried with the end of th rod stuck in a large flat cork. The lead should not be touched before weighing. The result was satisfactory. The cathode increased in weight slightly, although the current was stopped for five seconds early in the electrolysis.

PURE LEAD SAMPLE.

Lead Present,	Found		Lead Deposited on Cathode	Error Milligrams	Time	Speed
Grams	PbO_2	Pb (Factor 0.866)			Minutes	R. P.M.
0.4990	0.5730	0.4962	0.0021	—0.7	25	1000

The factor for lead in the dioxide deposit varies considerably with the conditions. Smith recommends the factor 0.8643 when using a sand-blasted platinum dish as anode and rotating the cathode. In this work the theoretical factor 0.866 comes nearer the real condition, and has been used throughout. The temperature of 130° to 135° is sufficient to dry the deposits in 15 minutes. Alcohol and ether were never used previously to drying the lead, although they were always applied to the copper deposits.

PURE LEAD AND COPPER.

A series of experiments was made with varying proportions of pure lead and copper.

The speed was kept between 400 and 700 R.P.M.

$N.D._{100} = 8$ amperes at 6 volts for the cathode, while the anode, with surface of only 20 sq. cm., had a higher density $N.D._{100} = 40$.

One cc. of 25 per cent sulphuric acid and nitric acid

*Paper presented at the 24th General Meeting of the American Electrochemical Society, at Denver, Col., Sept. 9-11, 1913.

(sp. gr. 1.42) varying from 3 to 6 cc. were added to the contents of the dish before passing the current.

	Weight of Lead Dioxide			Copper		
	Present	Found	Error Milligrams	Present	Found	Error Milligrams
A	0.0107	0.0104	— 0.3	0.6530	0.6526	— 0.4
B	0.0375	0.0374	— 0.1	0.6530	0.6530	0.0
C	0.1072	0.1064	— 0.8	0.6530	0.6540	+ 1.0
D	0.1072	0.1070	— 0.2	0.6530	0.6535	+ 0.5

APPLICATION TO BRASS ANALYSIS.

(a) *Preliminary Treatment.*—Five grams of brass drillings free of oil, are weighed into a tall 1-litre beaker. Ten cc. of water and 20 cc. strong nitric acid are introduced. All the metal is dissolved in from 5 to 15 minutes. About 150 cc. of hot water is added, and the whole boiled briskly for 5 minutes to expel nitrous fumes. Much turbidity indicates more than a trace of tin, and the meta-stannic acid is filtered off, ignited and weighed. Ordinarily mere traces of tin are present, and the solution is made up to exactly 250 cc., and 50 cc. withdrawn for electrolysis. This sample corresponds to 1,000 grams of brass and the weight of copper will correspond to per cent directly.

(b) *Electrolysis.*—The platinum dish should have a capacity of at least 100 cc. but it need not weigh more than 40 grams. The dish anode is advantageous, but a spiral wire anode will do if the surface has been platinized. Gauze has not been tried under these conditions, but a flat, circular gauze anode would be perfectly applicable. A spiral anode having 5 sq. cm. submerged surface will hold 0.0900 gram of lead dioxide. This limit is seldom exceeded, the average lead percentage being below 4 per cent, or corresponding to 0.05 gram of dioxide.

To the 50 cc. sample 4 cc. of strong nitric acid and 1 cc. of 25 per cent sulphuric acid were added, and the current of 8 amperes at 6 volts applied for 30 minutes. The cover glasses were generally washed after about 7 minutes, when the blue color had faded from the solution. The washing was twice repeated, and the siphoning was conducted as recommended in "Electro-Analysis," by E. F. Smith.

At the time of washing, the anode must not be nearer the dish than ½-inch, hence the dish is lowered at some time during the latter part of the electrolysis. Rotation is not stopped until the water has been shaken off by rotation in the air. The deposit is dried at 130° C. for 15 minutes. Constant weight is reached in this time, as is shown by further drying and re-weighing.

In case a gray spot of zinc forms on the copper, due to not keeping the anode distant ½-inch while washing a little hydrochloric acid may be used without impairing the copper deposit appreciably.

Iron is determined in the siphonate by a volumetric method, while the zinc in routine work is taken by difference.

Many analyses of brass have been run, but few results have been obtained using both methods on the same metal. After working with the method, and testing the siphonate with hydrogen sulphide, sufficient confidence was gained for its adoption, and the old process of electrolyzing for copper and lead separately was abandoned.

Analysis when lead is in comparatively large proportions, i. e., any amount more than ¼ that of the copper. The nitrate solution should contain no unnecessary free acid. Sulphuric acid is added in excess of the lead present. After the lead sulphate has settled, the solution may be decanted off, and more nitric acid added immediately to prevent further precipitation of lead sulphate. The bulk of the lead in the form of sulphate after washing several times with water by decantation is free of copper, and may be dissolved in strong HNO_3 and electrolyzed independently. The copper solution is electrolyzed as previously described, enough nitric acid being added to give a concentration of 5 to 6 per cent. The necessity for evaporation of the lead siphonate for copper is thus avoided.

BRASS.

PRELIMINARY ANALYSES OF PURE METAL MIXTURES.

	Zinc	Weight of PbO_2			Copper		
	Present	Present	Found	Error Milligrams	Present	Found	Error Milligrams
1	0.340	0.1072	0.1070	— 0.2	0.6530	0.6526	— 0.4
2	0.125	0.0574	0.0582	+ 0.8	0.3270	0.3273	+ 0.3
3 (*a*)	0.340	0.0537	0.0543	+ 0.6	0.6500	0.6497	— 0.3
3 (*b*)	0.340	0.0537	0.0540	+ 0.3	0.6500	0.6490	— 1.0
4 (*a*)	0.250	0.1147	0.1145	— 0.2	0.6530	0.6520	— 1.0
4 (*b*)	0.250	0.1147	0.1148	+ 0.1	0.6530	0.6517	— 1.3
5 (*a*)	0.300	0.1730	0.1725	— 0.5	0.5630	0.5628	— 0.2
5 (*b*)	0.300	0.1730	0.1722	— 0.8	0.5630	0.5623	— 0.7

FOUNDRY BRASS SAMPLES.

	Zinc	Old	Weight of PbO_2			Copper		
	Present	Method	Found	Error Milligrams	Present	Found	Error Milligrams
6 (*a*)	0.320	0.0330	0.0322	— 0.8	0.6550	0.6550	0.0
6 (*b*)	0.320	0.0330	0.0329	— 0.1	0.6550	0.6544	— 0.6
7 (*a*)	0.320	0.0340	0.0340	0.0	0.6530	0.6530	0.0
7 (*b*)	0.320	0.0340	0.0539	— 0.1	0.6530	0.6520	— 1.0
7 (*c*)	0.320	0.0340	0.0331	— 0.9	0.6530	0.6535	+ 0.5

EFFECT OF OTHER METALS.

(a) *Zinc and Cadmium.*—Lead determinations were made in the presence of pure copper nitrate with and without zinc and cadmium nitrates. No harmful effects were observed. In fact, the complete precipitation of copper free from lead was facilitated by the presence of amounts of these metals when not in higher percentage than the copper. Small amounts of iron do not interfere. It was impracticable to try varying quantities of all the metals. Zinc was most often applied in the proportions of brass, 25 to 35 per cent. Larger quantities of iron and vanadium do not interfere with the complete deposition of copper, but they take the place of nitric acid, and unless the quantity of that acid be lowered there will not be the usual deposition of metal. Antimony and tin are so slightly soluble in nitric acid that they were not considered. Bismuth and arsenic interfere.

(b) *Bismuth.*—If the quantity of Bi be below 0.01 g. to 0.65 g. Cu, the copper is more readily precipitated, contains nearly all of the bismuth, and has a much deeper red appearance than usual. The quantity of nitric acid may be increased to advantage. Instead

of 4 cc., add 6 to 8 cc. More than 0.01 g. of Bi renders the copper loose and granular, and above 0.1 g. it is black. The lead is not contaminated if the acid concentration is increased and the deposits are small, but above 0.01 g. bismuth, the lead deposits to some extent on the cathode.

(c) *Arsenic.*—Varied amounts of arsenic in the form of arsenic acid were added to the elctrolyte. Below 0.02 gram, an added amount of nitric acid prevented any contamination of the copper. The lead peroxide had a gray appearance, and deposited partly with the copper if the quantity of arsenic exceeded 0.02 gram.

CONCLUSION.

The aim of this work has been to facilitate the analysis of brass. Enough general data have been obtained to warrant the application of the method to other alloys, provided they contain less than 2 per cent of arsenic or bismuth. These metals in small quantities act as reducing agents, and require the addition of a little more nitric acid, whereas iron has an oxidizing effect, and allows of less nitric acid being used.

A FUSION METHOD FOR THE DETERMINATION OF SULPHUR IN IRON AND STEEL.*

By FREDERICK H. FRANKLIN.†

The accurate determination of sulphur in iron and steel presents many difficulties, owing to the extremely variable and complex nature of the iron-carbon alloys. It has been shown that sulphur combines with manganese in preference to iron. Therefore, in most commercial iron and steel alloys we have to deal with the former sulphide. It has been found that the insoluble residue left on dissolving iron for the sulphur determination usually contains some sulphur and this must be determined in accurate work. It is also well known that when much cementite is present volatile compounds of sulphur and carbon are formed which are difficult to oxidize and so escape estimation. It may readily be seen therefore that the method employed should be capable of giving a correct measure of the total sulphur no matter whether it exists in one or all of the above combinations.

For the purposes of this paper it will be sufficient to describe briefly one representative from each of the two principal classes into which the sulphur methods may be divided.

The volumetric or evolution method is in very general use and is usually modified by its advocates to meet the existing conditions. The gravimetric or oxidation method possesses some advantages over the former and is believed to be the most accurate method now in use. Both of these methods have a multitude of modifications and the mere statement that sulphur was determined by the volumetric or by the gravimetric method is no proof that the figures reported are the most accurate obtainable by the class chosen.

The Volumetric or Evolution Method.—In its simplest form this method consists of dissolving the metal in 1.1 sp. gr. hydrochloric acid and passing the evolved gases through an ammoniacal solution of cadmium chloride. The mixture of cadmium sulphide and dilute ammonia is acidified with hydrochloric acid and titrated with a solution of iodine that has been standardized either against sodium thiosulphate or iron of known sulphur content. The chief advantages of this method lie in its rapidity and the index of the amount of sulphur afforded by the precipitated sulphide. For most irons and steels this method when properly carried out gives results that agree fairly well with those obtained by the gravimetric method.

To overcome the shortcomings of the method some authors propose annealing the drillings which by changing cementite, martensite, etc., into pearlite, prevents loss of sulphur as volatile compounds. It is also claimed by other writers that by passing the evolved gases through a red hot tube, the carbon-sulphur compounds are broken down to hydrogen sulphide.

A German Commission,[2] appointed by the Verein Deutscher Eisenhüteenleute to investigate the determination of sulphur in iron and steel, considered the use of hydrochloric acid of 1.19 sp. gr. absolutely necessary and that when used, the passage of the evolved gases through a red hot tube can be dispensed with.

T. Gifford Elliot,[3] in the Journal of the *Iron and Steel Institute,* combines the annealing and strong hydrochloric acid modifications and when titrating runs in an excess of standard iodine solution and titrates back with sodium thiosulphate.

The Gravimetric or Oxidation Method.—This is usually executed by dissolving the iron or steel in strong nitric acid. The solution is evaporated to dryness, baked, redissolved in strong hydrochloric acid, diluted, filtered and the sulphur precipitated as barium sulphate. This method is also modified at several stages,[4] the most important of which are solution in nitric acid and removal of excess acid before precipitation of barium sulphate.

Potassium bromide and chlorate are used by Noyes to prevent loss of sulphur during solution and the same author separates the iron by ammonia before precipitating the barium sulphate. In nearly all methods, however, the barium sulphate is formed in the presence of a large amount of ferric chloride and no attention is paid to the iron retained by the barium sulphate.

That the oxidation method has many failings is indicated by the numerous attempts to overcome them by

*From the Journal of Industrial and Engineering Chemistry.

†Cf. Saunders and Franklin. Official chemists for the New England Foundrymens' Asociation.

[1]Carnot and Goutal, Compt. rend., 1897, 125; J. C. S., 1897, 72.

[2]Schwefelbestimmung in Eisen u. Stahl, Stahl. u. Eisen, 23 Jahr., Nr. 8.

[3]"The Volumetric Estimation of Sulphur in Iron and Steel," J. I. S. I., 1911, No. 1.

[4]Bamber, J. I. S. I., 1, 319 (1894).

modifications. This is one of the principal reasons that led to the development of the new method which is called the Fusion Method and is the result of a search for a method capable of giving accurate results with any kind of iron. It was desired that solution of the iron be effected without the use of acids and that the sulphur be precipitated as barium sulphate without the presence of iron salts.

Having observed that the carbonaceous residue obtained by the solution of iron in copper-potassium chloride solution contained sulphur, an experiment was carried out to learn how much of the total sulphur it contained.

A few grams of cupola iron (pig iron remelted in the cupola) were dissolved in a solution of copper-potasisum chloride and filtered through asbestos. The carbonaceous residue was mixed with sodium carbonate, sodium peroxide and a little sugar, then ignited by a hot wire. The aqueous solution of the fusion was acidified with hydrochloric acid heated to boiling and the sulphur precipitated by barium chloride. The results were surprising, giving a greater percentage of sulphur than was obtained by the volumetric method.

A large number of experiments were carried out and all results agreed closely with the gravimetric figures. A search through the literature on sulphur was made and the nearest approach to this method was found in an article by C. Meineke in *Zeitschrift für angewandte Chemie*.[5] The author dissolves the iron by boiling with a solution of copper-ammonium chloride, acidified with hydrochloric acid, and then after filtering off the insoluble, dissolves it in an oxidizing acid and, after evaporating to dehydrate silica, filters and precipitates sulphur as barium sulphate.

THE FUSION METHOD.

This method is given with considerable detail, not because this is necessary for accurate results but because of a desire to assist those who are not familiar with the technique of the operations involved.

The sample should be prepared with care and should be moderately fine; drillings made slowly with a rather dull drill are best.

SOLUTIONS, ETC., REQUIRED FOR THE FUSION METHOD.

Copper-Potassium-Barium Chloride Solution. — Dissolve 600 grams of copper-potassium chloride in warm water, add 30 cc. of hydrochloric acid, 30 cc. of barium chloride solution, and dilute to 1600 cc. After standing 24 hours, filter through asbestos.

Sodium Peroxide is practically free from sulphur.

Anhydrous Sodium Carbonate is free from sulphur.

Barium Chloride Solution of 20 per cent strength.

Hydrochloric Acid, C. P., has a density of about 1.19.

Dilute Hydrochloric Acid.—Add 100 cc. of hydrochloric acid to 900 cc. of distilled water.

Asbestos Suspension.—The acid-washed fiber is ignited and again washed with dilute hydrochloric acid and kept suspended in water.

Dissolve 3 grams of sample in about 120 cc. of copper-potassium chloride solution containing barium chloride, by means of a suitable stirring device. A Juno motor in series with an incandescent lamp gave excellent service. Allow the solution to stand about thirty minutes, then decant upon an asbestos pad formed in a porcelain Gooch crucible, using suction to hasten filtration. Wash the residue into the crucible by means of a fine stream of dilute hydrochloric acid, using as little as possible. After acid has run through, add just enough fine asbestos suspension to cover the carbonaceous residue. Finish washing with 15 to 20 cc. of warm water.

After all has passed through, wash down the sides of the crucible with a few drops of alcohol. Remove the pad and residue with tweezers, an operation easily accomplished if the crucible has a removable bottom. Separate the asbestos as completely as possible and dry the black residue at a temperature slightly under 100° C. for about 15 minutes.

Weigh 3 grams of anhydrous sodium carbonate and mix with it the dried residue by means of a small glass mortar and pestle.

Transfer to a nickel crucible of 20 cc. capacity and incorporate 3 grams of sodium peroxide. Place the covered crucible over a small flame and heat till the gentle oxidation is completed and the melt is quiet and homogeneous. This operation requires only about 2 or 3 minutes and should not be continued longer or much nickel will be dissolved.

While the melt is solidifying, cause it to cover the sides of the crucible. Rinse off the outside of the crucible and place in a small beaker containing 50 cc. of hot water and warm until the fused mass is detached. After removing and rinsing the crucible, add 15 cc. of hydrochloric acid, using precautions to prevent loss.

After boiling this solution until clear, evaporate to dryness in platinum and heat in oven at 130°-135° C. to dehydrate silicic acid. Dissolve the residue in 50 cc. of distilled water containing 1 cc. of hydrochloric acid, filter and wash until a filtrate of about 90 cc. is obtained. Heat to near the boiling point and add 7 cc. of hot 20 per cent barium chloride solution, drop by drop, keeping the temperature near the boiling point. A Schuster dropping flask (shaped like a tiny retort) is convenient for this purpose. Keep the beaker with the precipitate warm for some time and allow to stand over night or about 15 hours. Collect the barium sulphate on an asbestos pad in a platinum Gooch crucible, wash, ignite and weigh.

With steels and low silicon irons the method may be shortened by omitting the evaporation to remove silica, if the amount of asbestos fused with the residue is not large. Should a slight precipitate of manganese dioxide appear it may be dissolved by the addition of a minute crystal of tartaric acid, which usually produces a sparkling light green solution.

[5]Abstract in Chem. News, March 1, 1889.

In the following table of results, those obtained by the volumetric method are marked *v*, and those by the gravimetric, *g*:

TABLE OF RESULTS.

Sample	Percentage Sulfur	Percentages sulfur: Fusion method	Percentages sulfur: Other methods
Bureau of Standards			
C renewal	0.035	0.039	0.032 *g*
B	0.039	0.038	0.042 *g*
B	0.039	0.044	0.036 *v*
B	0.039	0.041	....
C 2nd	0.034	0.032	....
C 2nd	0.034	0.036	....
C 2nd	0.034	0.043	....
D 3rd	0.035	0.036	0.041 *g*
D 3rd	0.035	0.041	0.036 *v*
0.4 Bes. steel	0.118	0.124	0.115 *a*
Am. Fdy. Assn., A	0.056	0.057	
	Number		
Cupola iron	38676	0.177	0.155 *v*
	21678	0.123	0.113 *v*
	37485	0.108	0.105 *v*
	39991	0.102	0.097 *v*
	39345	0.160	0.130 *v*
	34345	0.116	0.101 *v*
	40103	0.165	0.147 *v*
	16519	0.128	0.105 *v*
	16450	0.124	0.107 *v*
	16419	0.126	0.119 *g*
	30253	0.095	0.092 *v*
	16519	0.128	0.116 *g*
	41173	0.131	0.096 *v*
	39345	0.170	0.130 *v*
Pig irons (Cu = 0.76%)		0.054	0.054 *g*
	30402	0.053	0.040 *v*
	29765	0.075	0.074 *g*
	29949	0.047	0.047 *v*
	29949	0.051	....
	2789	0.095	0.084 *g*
	18169	0.049	0.044 *g*
White irons—			
Chilled roll	.....	0.170	0.160 *g*
Malleable, as cast	41652	0.148	0.095 *v*
Malleable, as cast	41780	0.168	0.128 *v*
Low sulfur steel	....	0.014	0.010 *g*

Numerous blank tests were run, using regular amounts of reagents under the same conditions as the analyses themselves and the average amount of sulfur found was 0.0013 per cent.

EXPERIMENTAL.

It was thought at first that all the sulphur would not be obtained in the carbonaceous residue but my earliest experiments always gave results that agreed well with the analyses of the Bureau of Standard samples. Carnot and Goutal[6] have shown that "When iron or steel is heated with dilute acids, almost all the sulphur is converted into hydrogen sulphide but when the solvent is a neutral or faintly acid solution of copper-potassium chloride all of the sulphur remains in the residue, partly as ferrous sulphide, but often mainly as cupric sulphide. Direct examination shows that the copper solution has no effect on ferrous sulphide and it fellows that the sulphur is partly present in the metal as some other sulphide. Direct examination also shows that the sulphur in combination with copper in the residue is equivalent to the manganese in the iron or steel. Hence part of the sulphur is in combination with manganese as manganous sulphide."

Should any sulphur pass into solution it will immediately form barium sulphate with the excess of barium chloride present in the solvent. Moreover, the solvent is saturated with barium sulphate so that precipitation is immediate.

A few experiments in support of these views and some others which show the effect of free hydrochloric acid on the solubility of barium sulphate are given below:

Barium Sulphate is Carried Down by Carbon.

I—4 cc. of $BaCl_2$ solution were added to a 1 gm. sample of shot iron while dissolving in copper-potassium chloride solution. After filtering as usual, 2 grams of granular zinc were added and the solution rotated rapidly till clear. No precipitate was found in hours.

II—Sample treated as in preceding experiment but 2 cc. of N/H_2SO_4 were added before filtering. Copper was removed by granular zinc but no precipitate found.

III—To the last test (II), 2 cc. $N/20$ H_2SO_4 were added and a precipitate formed immediately.

Barium Sulphate is Insoluble in the Ferrous-Cuprous Solution.

IV—2 grams of pig iron dissolved in CuKBaCl solution gave 0.096 per cent S or 0.0140 gram $BaSO_4$.

V—2 grams of pig iron dissolved as before and 2 cc. of $N/20$ H_2SO_4 added, stirred 5 minutes longer and allowed to settle forty-five minutes on oven. $BaSO_4$ precipitate could be distinctly seen. The iron contained the equivalent of 0.0140 gram of $BaSO_4$ and 0.0116 gram was added giving a total of 0.0256 gram and 0.0245 gram was found. Results but 0.001 gram low, showing practically no loss of $BaSO_4$.

Barium Sulphate is Precipitated Immediately and Completely.

VI—2 grams of high sulphur iron (S = 0.27 per cent) were dissolved in CuKBaCl solution. Remained on oven one hour and filtered. The filtrate divided into two portions.

A—Placed in long Nessler tube and kept on oven 24 hours. No precipitate visible. After filtering through Gooch, no gain in weight. Absence of $BaSO_4$.

B—Placed in long Nessler tube and 1 cc. of H_2SO_4 (= 0.006 gram of $BaSO_4$) added. After standing on oven 2 hours, precipitate of $BaSO_4$ was distinctly visible. After 24 hours, filtered on Gooch and weighed 0.007 gram. The residue was tinged with iron oxide.

To Learn if $BaSO_4$ Separates from High Sulphur Samples on Long Standing.

VII—3 samples of cast iron, 47006-47007-47008, were carried through for sulphur, using CuKBaCl solution and gave:

No.	Percentage sulphur: Fusion method	Percentage sulphur: Vol. method
47006	0.136	0.114
47007	0.121	0.109
47008	lost	0.106

The filtrates above stood on the oven for 4 days, then were filtered through paper and carefully washed with dilute HCl and water.

They weighed as follows:

47006..... 0.0014 gram
47007..... 0.0050 gram
47008..... 0.0025 gram

[6] Loc. cit.

These tests deposited basic salts while standing on oven, to dissolve which they were treated twice with 2 cc. of HCl, but this did not prevent appearance of basic salts. On filtering no indication of $BaSO_4$ was noted and only an iron stain remained on paper. The 3 filter papers were ignited and weighed separately, then combined and fused with Na_2CO_3, the solution made faintly acid with HCl and evaporated to crystals. The residue was dissolved in 10 cc. of water and only a slight flocculent precipitate was visible (SiO_2?).

Effect of Hydrochloric Acid on the Solubility of Barium Sulphate.

VIII—Four solutions were prepared each containing 3 grams of sodium carbonate and sodium peroxide, made just acid to methyl orange with HCl. 5 cc. $N/20$ H_2SO_4 were added to each (= 0.0294 gram $BaSO_4$).

HCl was added in increasing amounts to each test as follows:

	1	2	3	4
HCl	0.25 cc.	0.50 cc.	1.00 cc.	2.00 cc.

Tests were heated to boiling and slowly precipitated with 7 cc. hot $BaCl_2$ solution, using a Schuster bottle. Volume = 100 cc. All precipitates were granular and settled rapidly. All precipitates were collected on a carefully prepared asbestos pad and the following results were obtained:

	1	2	3	4
Gram $BaSO_4$.....	0.0303	0.0304	0.0290	0.0312

A METHOD FOR THE DETERMINATION OF PHOSPHORUS IN VANADIUM STEEL AND FERRO-VANADIUM.*

By C. F. SIDENER and P. M. SKARTVEDT.

This paper embodies the adaptation of some well-known reactions to the determination of phosphorus in vanadium steel and ferro-vanadium, together with results obtained by the method, which is as follows: The sample is dissolved in dilute nitric acid. If an insoluble metallic residue remains, a little hydrochloric acid is also added. The solution thus obtained is evaporated to dryness and baked until the nitrate of iron is decomposed. The residue is dissolved in concentrated hydrochloric acid and about 0.02 gram of aluminium in the form of aluminium chloride is added. The solution is nearly neutralized with ammonia, heated almost to boiling, and the iron reduced by the gradual addition of a concentrated ammonium bisulphite solution with stirring. The reduction is best accomplished by keeping the solution slightly acid until nearly reduced, and then adding ammonia until a slight permanent precipitate of iron hydroxide remains after vigorous stirring, finally dissolving the precipitate with a few drops of ammonium bisulphite. To the solution, now smelling quite strongly of sulphur dioxide, one or two cc. of phenylhydrazine[1] are added drop by drop with stirring. If no precipitate appears, a few drops of ammonia are added until a slight permanent precipitate is formed. Then a few drops more of phenylhydrazine are added to complete the precipitation. The solution is boiled about two minutes, allowed to settle and filtered.

This precipitate consists of aluminium phosphate, aluminium hydroxide and more or less of the vanadium. After washing with hot water until the washings show no cloudiness when tested with mercuric chloride, the precipitate is dissolved off the filter into the original beaker with dilute nitric acid.

In the nitric acid solution containing the phosphorus and vanadium, the latter is oxidized by the addition of a little hydrogen peroxide, and then a slight excess of sodium carbonate is added. The solution is boiled for about five minutes and the phosphorus precipitated as aluminium phosphate by gradually adding dilute nitric acid until the solution no longer gives an immediate brown tinge to turmeric paper.[2] It is important that this point be very carefully noted. The precipitate is filtered off and washed with a 1 per cent

TABLE I.

Iron taken, 1 gram; vanadium, 6.75 mg. in first 11 and 27 mg. in last four experiments; phosphorus, 2 mg. The actual weight of phosphorus varied from 1.38 mg. to 2.40 mg., but for convenience of comparison all were calculated to a 2 mg. basis.

Milligrams of phosphorus found.				
2.01	1.98	2.01	2.07	1.97
2.03	2.13	2.00	2.01	1.99
2.03	1.95	1.97	2.08	1.98

TABLE II.—RESULTS ON A BUREAU OF STANDARDS VANADIUM STEEL, CONTAINING 0.15 PER CENT VANADIUM AND 0.035 PER CENT PHOSPHORUS.

No.	Grams steel taken.	Percentage phosphorus found.
1.....	1.2377	0.0353
2.....	0.8329	0.0352
3.....	2.9114	0.0340
4.....	2.5538	0.0350
5.....	3.5430	0.0347
6.....	3.9635	0.0356

TABLE III.—RESULTS ON TWO BUREAU OF STANDARD STEELS TO WHICH WAS ADDED VANADIUM IN VARIED AMOUNTS FROM 0.5 PER CENT UP TO 30 PER CENT OF THE WHOLE WEIGHT TAKEN.

	Steel taken Grams	Percentage vanadium added	Percentage phosphorus in the steel	Percentage phosphorus found
1.....	1.4102	0.5	0.093	0.096
2.....	1.5759	0.5	0.093	0.092
3.....	1.4749	0.5	0.093	0.0917
4.....	1.5297	0.5	0.093	0.094
5.....	1.5090	0.5	0.093	0.101
6.....	1.5015	0.5	0.093	0.108
7.....	1.5022	0.5	0.093	0.097
8.....	1.5019	0.5	0.093	0.089
9.....	1.0462	1	0.112	0.110
10.....	1.0088	1	0.112	0.113
11.....	1.2064	1	0.112	0.111
12.....	1.1623	1	0.112	0.109
13.....	1.0244	5	0.112	0.107
14.....	1.0469	5	0.112	0.119
15.....	0.9995	5	0.112	0.113
16.....	1.0092	20	0.112	0.116
17.....	1.0055	20	0.112	0.111
18.....	1.0040	20	0.112	0.111
19.....	1.0077	30	0.112	0.102
20.....	1.0095	30	0.112	0.103
21.....	1.0107	30	0.112	0.106
22.....	1.0092	30	0.112	0.114

*From the Journal of Industrial and Engineering Chemistry.

[1] Hess and Campbell, J. Am. Chem. Soc., 21, 776.

[2] C. M. Johnson, "Chemical Analysis of Special Steels," p. 26.

solution of ammonium nitrate. It is then dissolved off the filter into an Erlenmeyer flask with dilute nitric acid and a little hydrogen peroxide added, which will produce a deep red color if much vanadium is present and a pinkish yellow if but a trace is present. If this test shows the presence of even a trace of vanadium, another precipitation with sodium carbonate and nitric acid is necessary. The number of precipitations required to separate the phosphorus from the vanadium depends upon the amount of vanadium in the sample. For those containing up to 1 per cent a single precipitation is sufficient; 1 to 5 per cent, two precipitations; and from 5 to 30 per cent, two and often three.

To the nitric acid solution is now added ammonium molybdate to precipitate the phosphorus which is determined by the permanganate oxidation method in the usual manner. If the vanadium has not been completely separated from the phosphorus it will be indicated by the orange color of the ammonium phosphomolybdate precipitate which is quite characteristic; also by the tendency of the precipitate to form quickly and adhere to the glass.

Results obtained by this method are given in the accompanying tables: Table I shows the results obtained from a mixture of standard solutions containing iron, phosphorus and vanadium in proportions approximately those found in vanadium steels.

Although some of the results in the above tables are not as concordant as might be desired, yet it is believed that they may be taken as satisfactory for so troublesome a determination.

ABSORPTION AND REACTION TOWERS FOR CHEMICAL WORKS.*

Rudolf Heinz,[1] after reminding the reader that the main requirements for good absorption are greatest possible surface per cubic foot of filling, good mixing of gas, and the correct proportioning of the ratio between the section of the tower and the net section free for the passage of the gases, points out that the intending purchaser has a large variety of tower packings to select from. The days of coke as a filling material except in certain very special cases, are numbered, and it has long been established that a small tower with good packing will accomplish the same amount of work as a large coke tower. Plain acid-proof bricks, prism-shaped bricks, triangular rhombohedral, and trough-shaped bricks, and rings of various kinds, have all been tried in practice, and all have been found to have a common defect, namely, that they occupy a large percentage of the volume of the tower and leave insufficient "absorption space" for the gases.

Heinz states that the most successful tower packing of recent years were the "Guttmann" hollow balls; the success of these was due to their very high "free space" (the percentage of the cubic capacity of a tower which remains free for gases). Millions of these balls were sold, but they could not come into general use on account of their high cost and because they were unsuitable for large towers and gases containing dust.

The latest type of filling material, "Guttmann" cells, are stated to be superior to even hollow balls, not only in regard to efficiency, but also because the cells are cheaper and possess a very high "free space." As shown in the illustration (Figs. 1 and 2), these cells, when built up in a tower, form in section a regular honeycomb structure, each four cells enclosing a reaction space corresponding to an additional cell. The whole of the tower is thus symmetrically divided up into a number of equal reaction spaces, and in such a manner that both the outer and inner surface of the cells are wetted, and must be traversed by the gases which are ascending and diffusing through the tower filling. The formation of separate streams of liquids or gases cannot occur when these cells are used. Fig. 1 shows diagrammatically four cells arranged in the same manner as if they were stacked in a tower, the path of the liquid being indicated by plain arrows and the probable course of the gases by means of circled arrows. Slots (a) are made in the top and bottom walls of the cells, the gases entering from below expand in the interior of the cell and pass out through the slots at the top. Each cell is provided at the sides with a number of projections (b), which rest against corresponding projections on the neighboring cells, and at the same time, form the slots for the reaction space formed by four adjacent cells. The side walls of the cells being very steep, render it practically impossible, Heinz claims, for solid matter to collect on them, while, if necessary, the cells may be readily and quickly flushed down and cleaned. For extremely dusty gases—such, for example, as pass through a Glover tower—the lower third of the tower may be filled with large slabs or bricks in the usual way. The "active surface" of the large cells is 15 square feet per cubic foot.

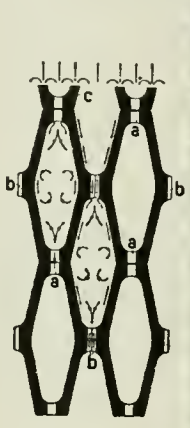


Fig. 1.

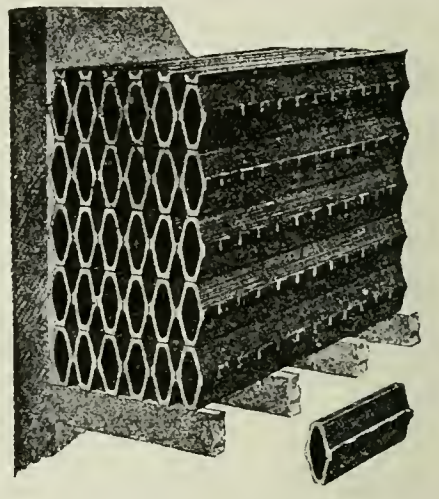


Fig. 2.

*From Journal of Industrial and Engineering Chemistry.
[1]Z. angew. Chem., 26, No. 57, 419; see also Chem. Trade J., 53, 75.

THE LABORATORY

METHODS OF ANALYSIS USED IN THE LABORATORIES OF THE ARMOUR INSTITUTE OF TECHNOLOGY.

The Analysis of Silicates—(Continued.)

Metals Precipitated as Sulphides (Zn, Ni, CO, and Cu).—The filtrate from the precipitation of iron, alumina and manganese (etc.) may contain traces of nickel, zinc, cobalt and copper. If their presence is suspected they may be removed as follows: To the solution (which will be alkaline at this point) is added two or three c.c. of a freshly prepared solution of ammonium sulphide, and the whole then saturated with hydrogen sulphide. This operation should be carried out in an Erlenmeyer flask, and after complete saturation with the gas, the flask should be stoppered and allowed to stand some hours (preferably over night) to assure complete precipitation. The precipitate of sulphides is filtered off and washed with hydrogen sulphide water. If very minute (as it will be in most cases), the paper may be carefully burned and the precipitate ignited in a porcelain crucible, the residue being weighed and reported as hydrogen sulphide metals. If desired, these metals may be separated. In most cases they will be either entirely absent or inconsiderable.

The filtrate after the separation of the sulphides contains calcium and magnesium (possibly barium and strontium) and the alkali metals. Of these, calcium and magnesium are always determined. Any strontium always accompanies the calcium and is seldom separated from it.

The Determination of Calcium.—The combined filtrates obtained above should not be more than 200 c.c. in volume. If greater than this, it should be concentrated. It is not generally necessary to remove ammonium salts by evaporation and ignition if the previous operations have been carefully carried out. This solution is brought to boiling and to it is added a slight excess of ammonium oxalate and the whole boiled for about five minutes. The precipitate of CaC_2O_4 is allowed to settle and is then thrown upon a special "baryta" filter paper and washed several times with hot water. If the filtrate is not perfectly clear, it must be re-filtered through the same paper until it is. As it is necessary to reprecipitate the calcium oxalate to assure its freedom from magnesium and enclosed sodium salts, it is unnecessary to remove all of the precipitate from the beaker. After the partial washing of the precipitate, the filtrate is removed and the precipitate dissolved in the least possible volume of 1:2 hydrochloric acid (hot) from a wash bottle, the solution being caught in the beaker wherein the original precipitation was made. The filter is washed free from chlorides and a little ammonia solution poured over it. The solution is then made alkaline and about one c.c. of oxalate added, the whole being boiled until the calcium oxalate settles readily, when it is thrown upon a fresh paper and washed with hot water, washing not being prolonged unnecessarily. The precipitate may be treated by either of the following methods: (a) Gravimetric. The calcium oxalate precipitate is transferred to a weighed platinum crucible, and the paper ashed. The crucible is then covered and heated for five minutes over an inclined blast flame or for a somewhat longer time (20 minutes) over the Meker burner. This converts all of the oxalate to oxide, and the residue is weighed as such. It is well to repeat the heating and check the weight, as the lime is very hydroscopic and must be weighed rapidly. (b) Volometric. The volumetric method depends upon the solution of the oxalate in dilute sulphuric acid and the titration of the liberated oxalic acid by standard potassium permanganate.

The precipitate of oxalate is rinsed off of the paper into a 200 c.c. beaker by the aid of the wash bottle, and the beaker and contents placed under the filter paper, which must be thoroughly washed with hot dilute sulphuric acid to free it from oxalate. More sulphuric acid is now added to the precipitate in the beaker and the whole warmed until solution is complete, when the permanganate solution is run in from the burette to the first permanent pink tinge. The reaction is slow in starting, but is rapid before the end point is reached. The solution should be hot throughout the titration. The calculation is as follows:

Since $2KMnO_4 = 5O = 10\,Fe = 5H_2C_2O_4 = 5CaO$,

Then $2Fe = 1CaO$,

and if the standard of the permanganate is expressed in terms of iron as is usually the case, its standard is calculated in terms of CaO from the proportion

$2(55.9) : 56 = Fe\ standard : \times$

$\times = Cao\ Standard.$

$$\frac{\text{vol. of permanganate} \times \text{CaO std.}}{\text{weight of sample}} \times 100 = \%\ CaO$$

Both methods are good. The gravimetric is slightly more accurate, but the volumetric is very reliable and much more rapid.

If it is desired to determine strontium (this is rarely necessary), the gravimetric method must be used, as the separation depends upon the conversion of the oxides to the dry nitrates and the extraction of calcium nitrate from the strontium salt by means of anhydrous ether and alcohol.

The Determination of Magnesium.—The combined filtrates from the double precipitation of the calcium oxalate contain all of the magnesium. The correct determination of this metal is always a matter of some difficulty, and care and close adherence to conditions are required. The following procedure yields good results. To the alkaline filtrate from the calcium (without evaporation and ignition to expell ammonium salts) is added a considerable excess of $NaNH_4HPO_4$ (microcosmic salt) in solution, and the whole allowed to stand over night. The precipitate contains all of the magnesium, but is not of a definite composition, being made up of the normal magnesium phosphate as well as the magnesium ammonium phosphate desired. It may or may not appear crystalline. This necessitates a re-precipitation in the absence of large quantities of ammonium compounds. To this end the precipitate is dissolved through the filter by means of dilute hydrochloric acid from a wash bottle, large excess of acid being avoided. After the filter has been washed free from chlorides, a few drops of microcosmic salt solution is added to the acid solution, and then drop by drop, with constant stirring, very dilute ammonia is added until precipitation commences. At the first appearance of precipitate the addition of ammonia is stopped and the solution stirred vigorously until the precipitation seems about complete, when the whole is made strongly alkaline with ammonium hydroxide of 0.90 sp. g. and allowed to stand over night again. This should give a complete precipitation of $MgNH_4PO_4$, crystalline. This precipitate is filtered off and washed with a dilute solution of ammonia. It is then dried, and the paper burned in a porcelain crucible. The grey residue is finally ignited in a muffle or (with the crucible covered) over a strong bunsen flame until white, and weighed as $Mg_2P_2O_7$, of which the MgO factor is 0.3624.

Fairly good results with but a single precipitation may be obtained as follows: The filtrate from the determination of calcium (which should not be too large in bulk) is acidified with hydrochloric acid and a considerable excess of microcosmic salt solution added. The whole is then warmed and the excess acid carefully neutralized by the addition of dilute ammonia solution, with constant stirring. The ammonia is sometimes added from a burette. When the precipitate appears, the addition of ammonia is stopped, but the stirring continued for a few minutes, when the whole is made strongly alkaline with ammonia and allowed to stand over night. The precipitate of $MgNH_4PO_4$, which will be fairly pure and definite, is treated as described above.

If greater speed in the determination of magnesia is demanded, the single precipitation as just described may be employed with the following modification, which will give satisfactory results in a couple of hours in most cases, although the long standing is always to be preferred. The precipitation is started exactly as described under the single precipitation method, and after the strong ammonia has been added the beaker is placed in a vessel containing ice water and the contents stirred for an hour or more by means of a mechanical stirrer. The larger the amount of magnesia, the easier it is to get complete precipitation. The filtrate from the $MgNH_4PO_4$ should always be kept for twelve hours, and if any further separation of precipitate takes place in that time, it should be collected and weighed, and added to the weight previously obtained.

The Determination of the Alkalies (Na_2O and K_2O).—The determination of potash and soda is made by the J. Lawrence Smith method, which is as accurate as any method and more convenient than others. In fact, it has practically replaced all other methods. It depends primarily upon the decomposition of the finely powdered sample by heating under the proper conditions with a mixture of calcium carbonate and ammonium chloride. The cintered mass is extracted with water, and the alkalies dissolved, together with a small quantity of calcium compounds. All of the silica, iron, alumina and magnesia (with the rarer elements as well) remain in the insoluble residue. This removal of the magnesia at the beginning is one of the great advantages of the method. The solution contains the alkalies, calcium hydroxide and calcium sulphate if the sample contained any SO_3. The calcium and sulphates are removed by precipitation, ammonium salts volatilized, the alkalies converted into chlorides, and after weighing as mixed chlorides, the potash is separated from the soda and weighed as potassium chlor-platinate, and the soda obtained by difference. The process is rather a tedious one, but not so difficult as it is frequently regarded.

The determination on Na_2O by this method is almost invariably too high. This is due to two principal causes, viz.: the reagents notable (1) the $CaCO_3$ is never entirely free from small quantities of sodium compounds, and (2) small amounts of soda are picked up from glass vessels throughout the process. Even where platinum vessels are employed, the hot water in the wash bottle, of which a large volume is used, always takes some alkali from the glass.

This being the case, it is always necessary to run a blank determination upon the reagents used, and make a constant correction upon all determinations. This correction will as a rule amount to from one to two milligrams of mixed chlorides when platinum vessels are used throughout. When porcelain and glass are employed, the weight may be greater.

The J. Lawrence Smith crucible is most convenient for the decomposition of the sample, but as this is of

platinum and from 25 to 40 grams weight, and has practically no other use than in this determination, it is not commonly met with in the analytical laboratory. The use of the ordinary platinum crucible in its place will therefore be described.

The sample for the determination of alkalies should be very thoroughly ground in an agate mortar before weighing. This is very important, especially when the ignition is carried out in an ordinary crucible where the probability of loss of alkalies by volatilization is greater than in the special crucible, making more careful heating and a somewhat lower temperature advisable.

The Process.—The sample of 0.5 gm. weight is placed in an agate mortar and there mixed by the aid of the pestle with an equal weight of pure ammonium chloride. To this is added nearly all of 4 grams of calcium carbonate and the mixture thoroughly ground together. The mixture is then transferred to a platinum crucible of not less than 25 c.c. capacity, which is provided with a well-fitting cover. Any of the mixture which adheres to the mortar is rinsed out by means of the small part of the 4 gms. of calcium carbonate not previously used. The crucible with its charge is fitted into a hole in a piece of stiff, heavy asbestos board in such a way that a little more than half of the crucible shows above the surface of the asbestos and less than half below. The charge must not fill more than half of the crucible. The asbestos board is then clamped in an inclined position, the crucible covered, and heated gently by means of a small bunsen flame, the tip of which is several inches below the crucible. This first heating causes decomposition of the ammonium chloride, with the absorption of HCl and the elimination of NH_3. When the odor of the latter is no longer detectible (this will take from ten minutes to half an hour), the temperature of the lower, exposed, part of the crucible is raised to a dull red heat and kept at that temperature for from two to three hours. This is a much longer time than is required when the J. Lawrence Smith crucible is used, and may be unnecessarily long in many cases with the ordinary crucible, but it is better to take plenty of time than to risk incomplete decomposition and repetition of the entire process. The material in the crucible after the ignition appears as a sintered cake, which comes loose from the crucible easily. It is transferred to a porcelain casserole and covered with water, the little remaining in the crucible being slaked and added to the main amount. The whole is then warmed with water until thoroughly disintegrated, and then the insoluble portion is filtered out and washed with hot water. Care should be taken at this, and other points of the process, to avoid large bulk of solution. The residue upon the filter is to be rejected, but it should be first tested for complete decomposition by dissolving it in hydrochloric acid. If no insoluble gritty residue is left, the decomposition was satisfactory. The solution (in a porcelain or platinum dish) is heated to boiling and to it a slight excess of ammonium carbonate added. The precipitate of calcium carbonate is redissolved in as little hydrochloric acid as possible and the $CaCO_3$ re-precipitated as before and washed. The combined filtrates contain all of the alkalies and a very little calcium, and sulphur as sulphate. They are evaporated to dryness on the water bath or on a heavy asbestos board and all ammonium salts removed by gentle ignition. This ignition may be carried out on a sand bath or the dish may be set inside of a slightly larger iron dish which is directly heated by a strong flame. Or the dish may be held directly over the flame. In this case the heat must be kept below redness to prevent loss of the alkalies. The former methods are better, though slower. The residue, free from ammonium salts, is taken up in a few c.c. of water and a few drops of ammonium hydroxide and a slight excess of ammonium oxalate added. If the presence of SO_3 is suspected, a drop of $CoCl_2$ should be added, the solution warmed and filtered, and the excess barium removed by $(Mfy)2CO_3$. Ammonium oxalate is then added. It is best to allow this to stand over night in a platinum dish to assure complete precipitation of the calcium oxalate. The CaC_2O_4 is filtered off and the filtrate caught in a weighed platinum dish. The solution is again evaporated to dryness and the ammonium salts expelled, the residue treated with a few drops of hydrochloric acid to assure the conversion of the alkalies to chlorides, re-evaporated, ignited and finally weighed. This, less the weight of the empty dish, gives the weight of the mixed chlorides $NaCl + KCl$.

Separation of Sodium and Potassium.—To the residue of mixed chlorides in the platinum dish is added a slight excess of the calculated amount of platinic chloride solution (0.1 gm. of chlorides will require about 0.3 gm. H_2PtCl_6, or 3 c.c. of a 10 per cent solution). The mixture is stirred with a small glass rod and evaporated on the water bath to a pasty consistency, but not to dryness. The residue should solidify upon cooling. Over this residue is poured about 10 c.c. of 80 per cent alcohol, the whole stirred, and the clear solution, after settling, poured through a small filter, as little as possible of the precipitate of K_2PtCl_6 being brought on the filter. The precipitate is washed several times by decantation until the washings and the paper are free from yellow color, and is then transferred to a weighed platinum crucible with the aid of a fine stream of hot water from a wash bottle. The little precipitate upon the paper is washed through the paper with boiling water into the crucible, and the solution is finally evaporated to dryness on the water bath, dried at 120-130°, and weighed. This gives all the potassium as K_2PtCl_6.

wt. $K_2PtCl_6 \times 0.3071 =$ wt. KCl,
wt. $(KCl + NaCl) -$ wt. $KCl =$ wt. NaCl,
wt. $KCl. \times 0.632 =$ wt. K_2O,
wt. $NaCl \times 0.5307 =$ wt. Na_2O.

A RAPID VOLUMETRIC METHOD FOR DETERMINING *o*- *m*- AND *p*-CRESOLS, THYMOL AND PHENOL.*

By L. V. REDMAN, A. J. WEITH and F. P. BROCK.

This method determines by one titration rapidly and accurately:

A. Ortho-, meta- and para-cresols or phenol.

B. The meta-cresol in the presence of *o*- and *p*-cresol.

C. Phenol in the presence of *o*- and *p*-cresol.

D. The meta-cresol, the phenol and the sum of the *o*- and *p*-cresols in any mixture of these compounds.

Three methods have been proposed for determining the cresols separately: (1) gravimetric,[1] weighing the ortho- and para-cresol as the dibrom-cresol-bromide, the meta-cresol as tribrom-cresol-bromide; (2) volumetric,[1] by Koppeschaar's solution, titrating back the unabsorbed bromine; (3) volumetric, by using a solution of iodine[2] in sodium acetate and titrating back the unabsorbed iodine with thiosulphate. This latter method does not serve for the quantitative determination of *m*-cresol.

A special method has been devised for determining *m*-cresol[3-4] in the presence of ortho- and para-cresol, by weighing the *m*-cresol as trinitro-*m*-cresol. The *o*- and *p*-cresol are oxidized away by strong nitric acid and trinitro-phenol is soluble if present in small amounts, *i. e.*, up to 10 per cent. The method, therefore, is reliable in the presence of *o*- and *p*-cresol and less than 10 per cent of phenol. H. Ditz[5] has given the following equations whereby the *m*-cresol present in a mixture consisting only of the three *o*-cresols may be determined—

$$x + y = a \qquad (1)$$

$$\frac{3\mathrm{Br}.x + 2\mathrm{Br}.y}{108.064} = b \qquad (2)$$

x = meta-cresol.

y = *o*- and *p*-cresol.

a = Wt. of mixture of cresols taken.

b = Wt. of Br. disappearing.

Br. = 79.97 grams.

The same equations will apply to a mixture of the *o*- or *p*-cresols and phenol. The equation (2) is modified for the formula weight of the phenol[6] as follows:

$$\frac{3\mathrm{Br}.x}{94.048} + \frac{2\mathrm{Br}.y}{108.064} = b \qquad (3)$$

x = the amount of phenol in the mixture taken.

Siegfried and Zimmermann[7] have criticized H. Ditz and Cedivoda's method and have shown that variable results from 2-20 per cent are obtained by brominating the cresols in an acid bromine solution. Their method varies from that of Koppeschaar's for determining phenol, only in the fact that one hour's time is allowed after the KI is added before the thiosulphate is run into solution. F. Russig and G. Fortmann[4] have also critcized Ditz and Cedivoda's method adversely. Ditz replied[8] to their objections and H. Ditz and F. Bardach[9] have published results at variance with Russig and Fortmann's conclusions.

Recently Pence[10] has shown that Koppeschaar's solution in an acid menstruum will determine quantitatively the meta-cresol as tribrom-meta-cresol. But the ortho- and para-cresols could not be determined either as the dibrom-cresols or the dibrom-cresol bromide, since the amount of bromine absorbed varied between the amounts required to form the dibrom-cresol and the dibrom-cresol bromide. Phenol, *o*-, *m*- and *p*-cresols all form the bromides in the presence of excess bromine, and if the precipitates are filtered off before the KI is added the reaction is nearly quantitative,[11] according to the following equations:

$$C_6H_5OH + 4Br = C_6H_2Br_3OBr$$

$$2\text{-}CH_3.C_6H_4OH + 4Br = 2\text{-}CH_3.C_6H.Br_3.OBr$$

and

$$1\text{- or } 3\text{-}CH_3C_6H_4OH + 3Br = 1\text{- or } 3\text{-}CH_3C_6H_2\text{-}Br_2OBR$$

The methyl group of the cresols will be slowly replaced by Br, if left in contact with excess Br. for several days. This has been shown by Autenrieth and Beuttel.[12] However, if the KI be added while the precipitate is present in the acid solution the free hydriodic acid reduces the bromide as follows:

$$C_6H_2Br_3OBR + HI = C_6H_2Br_3OH + Br + I$$

This reduction is complete for phenol[13] and meta-cresol;[14] consequently they may be determined accurately by adding bromide bromate to their acid solution, later adding KI and titrating back with thiosulphate. For the *o*- and *p*-cresol the case is somewhat different. The hydriodic acid does not reduce the bromide completely in a reasonable length of time, and as a consequence, all the results of the different investigators show that by this method more than 2 mols of bromine are absorbed for each mol of *o*- or *p*-cresol present. The authors of this paper have brominated the *o*- and *p*-cresols by the same method as described by Koppeschaar and modified[15] later for determining phenol, and the results have shown in every experiment that the bromine in the hydroxyl is gradually replaced by the hydrogen of the hydriodic acid, but the reaction is so slow that after an hour's time 6 to 40 per cent of the bromine still remains in the hydroxyl. For rapid and accurate work then, the acid bromine menstruum is not satisfactory in determining *o*- and *p*-cresols.

Recently a method was devised by Wilkie,[16] using a sodium bicarbonate and iodine solution for determin-

*From The Journal of Industrial and Engineering Chemistry.

[1]Ditz and Cedivoda, Z. angew. Chem., 12, 1873 (1899). Ditz and Bardach, Biochem. Z., 37, 272 (1911). Siegfried and Zimmerman, Biochem. Z., 29, 368 (1910).

[2]Pence, Journal of Industrial and Engineering Chemistry, 4, 518 (1912).

[3]F. Raschig, Z. angew. Chem., 13, 759 (1900).

[4]F. Russig and G. Fortmann, Ibid., 14, 157 (1901).

[5]H. Ditz, Ibid., 13, 1050 (1900). H. Ditz and F. Bardach, Biochem. Z., 37, 272 (1911).

[6]Siegfried and Zimmermann, Biochem. Z., 29, 368 (1910).

[7]Biochem. Z., 37, 272 (1911).

[8]Z. angew. Chem., 13, 1050 (1900).

[9]Biochem. Z., 37, 272 (1911).

[10]Journal of Industrial and Engineering Chemistry, 4, 518 (1912).

ing phenol. The authors of this paper have found the method quite accurate and when modified by diluting and continuous shaking the phenol may be determined to an accuracy of two parts in a thousand with a reaction period of only one minute. No subsequent filtering off of the precipitate is needed as in Wilkie's method. The short reaction period does not redden the precipitate enough to obscure the end point. Wilkie's method is a modification of Messenger and Vortmann's,[17] who used caustic soda in place of sodium bicarbonate. Messenger and Vortmann's results are not very satisfactory. Gardner[18] and Hodgson have modified Messenger and Vortmann's method so that only one iodine is absorbed by each mol of phenol.

Pence[19] has used an iodine solution for determining *o*- and *p*-cresol in the presence of sodium acetate. He found that this method would work satisfactorily for *o*- and *p*-cresol but not for the meta-cresol. The present authors have found iodine in sodium acetate too slow for a reaction period of one minute. (Pence recommends one hour).

The authors of this paper have not tested the gravimetric method for determining the cresols as dibrom-*o*- and *p*-cresol bromides and tri-brom-*m*-cresol bromide as the gravimetric is tedious and slow in the drying of the precipitates; the precipitate gives off the odor of bromine during drying and is at best not accurate within 1-2 per cent.[20]

Problem.—There remains then to discover a rapid and accurate volumetric method, which will serve equally well for the determination of each of the three cresols and phenol. If such a method can be found, it will be possible to determine by a single titration (1) the amount of *m*-cresol in a mixture of the three cresols, (2) the amount of phenol in a mixture of *o*-, *p*-cresol and phenol, (3) the amount of phenol and meta-cresol and the sum of the *o*- and *p*-cresols in a mixture of all four.

The Method.—Such a method has been found by determining the cresols in very dilute[21] solution, $N/100$, using an $N/30$ solution of iodine[22] dissolved in KI, adding the sodium bicarbonate[23] until the mixture is about ½ normal, shaking continuously the reacting mixture for one minute, acidifying and titrating back the excess iodine with thiosulphate.

EXPERIMENTAL.

Apparatus.—The only appliances needed are (1) standardized burettes. (2) ground stoppered ½ liter bottles, (3) 25 and 50 cc. pipettes and a shaking machine. The authors found that continuous shaking by hand of the bottles was as convenient as using the shaking machine when the "reaction period" was of only one minute's duration.

Solutions.—The solutions consisted of $N/30$ iodine, solutions containing 1/60 formula weight of each of the three cresols and phenol, $N/10$ thiosulphate, N sodium bicarbonate, 2 N sulphuric acid. The $N/30$ iodine was made up by dissolving 4.2 grams of resublimed iodine in a saturated solution of 15 grams KI, and making up to 1 liter. The standardization of the iodine solution was by arsenious acid. The thio-sulphate solution was prepared by dissolving 125 grams of sodium thiosulphate ($Na_2S_2O_3.5H_2O$) in 5 liters of water, allowing the solution to stand for one week and then standardizing it against the iodine.

The three cresol solutions were made up in each case by taking 1.801 grams of redistilled cresol and making it up to 1 liter. The cresols were from "Merck's highest purity" and were weighed out very carefully after redistilling.

Care was taken to exclude moisture and the samples were weighed out and made up accurately to volume. The N sodium bicarbonate solution was made by dissolving 84.1 grams of $NaHCO_3$ in 1 liter of water, the 2 N sulphuric acid by adding 56 cc. of concentrated bottle acid (sp. gr. 1.84) to about ½ liter distilled water, and making the total volume up to one liter. The two latter solutions need be only approximate.

Brominating the Cresols.—At the beginning of the research a bromide-bromate solution was used and acid added as in determining phenol. The bromination method was found to work quite satisfactorily for phenol and meta-cresol, but the amount of bromine absorbed by the *o*- and *p*-cresol at the end of the thiosulphate titration depends upon three factors:

(1) The excess of free bromine present.

(2) The length of time the bromine has acted upon the cresol solution.

(3) The time allowed for the hydriodic acid to act upon the brominated product, reducing the dibrom-cresol bromide to the dibrom-cresol.

If enough bromine be added the reaction is complete and dibrom-cresol bromide is formed and may be weighed as such.[24] But if the reaction in the presence of excess bromine proceeds for only one minute, the reaction is not complete. After allowing the hydriodic acid to reduce it for one minute and titrating back the excess iodine, 6 to 10 per cent of the hydroxyl still remains filled by bromine, giving an error in the determination of 3 to 5 per cent. The longer the hydriodic acid acts upon the product, the less bromine is left in the hydroxyl until after one hour's time the reduction has proceeded within 4 per cent of completion. The difficulty seems to be one of delayed diffusion. The precipitate, which is at first flocculent and fills the whole solution, condenses into a few small, solid wax-like particles which do not allow the hydriodic acid free

[11]Ditz and Cedivoda, Z. angew. Chem., 12, 1873 (1899). Autenrieth and Beuttel, Arch. Pharm., 248, 112 (1910). A. Seidell, Am. Chem. J., 47, 523 (1912).
[17]W. Autenrieth and F. Beuttel, Archiv. der Pharm., 248, 112 (1910).
[18]Rhodes and Redman, Journal of Industrial and Engineering Chemistry, 4, 655 (1912).
[19]Pence, Journal of Industrial and Engineering Chemistry, 4, 518 (1912).
[20]Ibid., 4, 655 (1912); 5, 389 (1913).
[21]Wilkie, J. S. C. I., 30, 398 (1911).
[17]Messenger and Vortmann, Ber. d. chem. Ges., 23, 2753.
[18]W. M. Gardner and H. H. Hodgson, J. Chem. Soc., 95, 1819 (1909).
[19]Pence, Journal of Industrial and Engineering Chemistry, 4, 518 (1912).
[20]Siegfried and Zimmerman, Biochem. Z., 29, 368 (1910).
[21]Redman and Rhodes, Journal of Industrial and Engineering Chemistry, 4, 655 (1912).
[22]Messenger and Vortmann, Ber., 22, 2753.
[23]Wilkie, J. S. C. I., 30, 398 (1911).

access to the unreduced bromide. The precipitate which originally occupied a space of ¼ liter shrinks (with partial solution)to a volume of less than 1 cubic millimeter, and when the colorless point is reached with the thiosulphate, one can see a continuous column of blue rising from the little granules at the bottom of the liquid, showing that the hydriodic acid is reducing (but very slowly) the dibrom-cresol bromide. Siegfried and Zimmermann[25] tried to hasten the reduction by warming the solution, but their attempts were unsuccessful. They recommend diluting the solution to 0.025 *N* and allowing 15 minutes for the "reaction period" without continuous shaking, then adding the KI, thoroughly shaking and titrating with thiosulphate. Their results show that the cresols may be determined by this method within 1 to 3 per cent. Our experiments confirmed their results. One difference was observed; if the shaking was continuous, the precipitate decreased in volume as described above and the determination was not accurate.

The bromine-acid method was abandoned in favor of the alkaline iodine method as the results are too dependent upon the dexterity and patience of the individual experimenters. Time was also a factor. The bromine method could not be hastened by shaking as in the case of phenol and meta-cresol for the precipitates of dibrom *o*- and *p*-cresol bromide coagulated into such small dimensions that rapid diffusion through it of the hydriodic acid was quite impossible. Allowing a reaction period of fifteen minutes and a reduction period for the bromide of one hour after the KI is added the method requires about one and one-half hours for determinations which are accurate only to 1 to 3 per cent. When this method is applied to a mixture of phenol and *o*- or *p*-cresol the error is aggravated and amounts to 3 to 21 per cent according to Siegfried and Zimmerman.[26]

DETERMINATION OF *o*- *m*-, AND *p*-CRESOLS SEPARATELY.

Each of the cresols was determined separately, according to the following method: About 50 cc. *N* sodium bicarbonate were poured into a ½ liter ground stoppered bottle, 100 cc. of water added, 15 or 20 cc. of the *N*/10 cresol were then run in from a standardized burette, and the volume was very carefully read. Enough *N*/30 iodine (40-70 cc.) to color the solution a permanent alkaline iodine color was then added. A reaction period of 1 minute was allowed, during which time the solution was shaken continuously, by hand or in the machine. Then 50 cc. 2 *N* sulphuric acid were added and after shaking thoroughly the excess iodine was titrated back with thiosulphate.

Tables I, II and III show the results for the three cresols.

Experiments 1 and 2 show that 20 per cent excess iodine and 10 minutes' "reaction period" do not increase the absorption of iodine over the 1 minute's reaction and 14 per cent excess free iodine in Experiment 9.

TABLE I.—DETERMINATION OF META-CRESOL.

Ex. No.	$NaHCO_3$ Cc.	Water Cc.	*N*/10 *m*-cresol Cc.	*N*/30 iodine Cc.	Reaction period Min.	2 *N* acid added Cc.	Thio Cc.	Per cent found of *m*-cresol
1...	20	100	20.00	70	10	25	4.20	100.0
2...	20	100	20.00	70	10	25	4.20	100.0
3...	20	100	15.00	50	10	25	2.26	100.0
4...	30	100	14.97	50	5	20	2.26	99.9
5...	50	50	15.02	50	5	30	2.20	100.0
6...	100	...	15.00	50	5	30	2.25	99.8
7...	(*a*)	...	15.00	50	5	15	3.20	93.4
8...	(*a*)	...	15.00	50	5	55	3.30	92.7
9...	50	100	15.00	50	1	30	2.20	100.2

(*a*) 100 cc. *N* sodium acetate were added in place of the bicarbonate.

For solutions, etc., see Table III.

Experiments 3 and 6 show that an increase of sodium bicarbonate from 1/6 *N* to normal does not increase the iodine absorption.

Sodium acetate was substituted for sodium bicarbonate in Experiments 7 and 8 which confirm Pence's[27] results that the *m*-cresol does not go over completely to tribrom-*m*-cresol in a short time in the presence of sodium acetate.

TABLE II.—DETERMINATION OF ORTHO-CRESOL.

Ex. No.	$NaHCO_3$ Cc.	Water Cc.	*N*/10 *m*-cresol.	*N*/30 iodine Cc.	Reaction period, Min.	2 *N* acid added Cc.	Thio Cc.	Per cent found of *m*-cresol.
10..	100	..	15.00	35.0	5	55	1.70	100.0
11..	50	50	15.00	39.9	5	30	3.37	99.96
12..	50	50	20.03	50.0	1	30	3.33	99.60
13..	50	50	20.00	50.0	1	30	3.41	99.90
14..	50	50	15.00	40.0	1	30	3.14	100.30

For solutions, etc., see Table III.

Experiments 10 and 11 show that the results are not affected by increasing the excess of free iodine from 11 to 22 per cent and Experiments 12, 13 and 14 show the absorption to be complete in 1 minute's time.

TABLE III.—DETERMINATION OF PARA-CRESOL.

Ex. No.	$NaHCO_3$ Cc.	Water Cc.	*N*/10 *m*-cresol Cc.	*N*/30 iodine Cc.	Reaction period, Min.	2 *N* acid added Cc.	Thio Cc.	Per cent found of *m*-cresol.
15...	50	50	20.00	50.3	1	30	3.55	99.7
16...	50	50	15.00	50.0	1	30	6.80	100.0
17...	50	50	15.00	40.0	1	30	3.29	100.0
18...	50	50	15.00	40.0	1	30	3.22	100.0

Thiosulphate = 0.0982 *N*. Sulfuric acid = 2 *N*. $NaHCO_3$ = *N*. Iodine = 0.0340 *N*. Temperature = 23° C.

Experiments 15, 16, 17 and 18 show that uniform

[24] Ditz and Cedivoda, Z. angew. Chem., 12, 1873 (1899).
[25] Siegfried and Zimmerman, Biochem. Z., 29, 368 (1910).
[26] Siegfried and Zimmermann, Biochem. Z., 29, 387 (1910).
[27] Pence, Journal of Industrial and Engineering Chemistry, 4, 518 (1912).

results are obtained by making the solution ½ *N* with sodium bicarbonate, allowing only 1 minute for the "reaction period." Excess of iodine (50 per cent in Experiment 16) did not increase the iodine absorption. It was consequently considered unnecessary to determine the effects of increased "reaction period."

It may be mentioned that the trio-iodo-meta- and di-iodo-para-cresols are precipitated as white flocculent masses before the solution is acidified. The di-iodo-ortho-cresols is precipitated as a red, more or less granular substance. On the other hand, iodo-phenol is not precipitated in *N*/2 sodium bicarbonate and the precipitate forms only on the addition of the acid. In *N*/10 sodium bicarbonate the precipitate forms and is not so red as the precipitate from the stronger carbonate solution.

TABLE IV.—DETERMINATION OF PHENOL BY IODINE-SODIUM-BICARBONATE SOLUTION.

Ex. No.	$NaHCO_3$ Cc.	Water Cc.	Phenol sol. Cc.	Iodine Cc.	Reaction period, Min.	2 *N* acid added Cc.	Thio Cc.	Per cent found phenol.
19.....	10	90	15	50	1	20	5.00	85.5
20.....	10	90	15	50	1	25	3.70	94.9
21.....	10	90	15	50	15	25	3.20	98.6
22.....	25	75	15	50	1	25	3.00	100.0
23.....	50	50	15	50	1	30	3.00	100.0
24.....	50	50	15	50	1	30	3.00	100.0
25.....	50	50	15	50	25	25	3.05	99.7
26.....	50	50	10	50	25	...	...	....

Iodine sol. = 0.03306 *N*. Others as in Table III.

Table IV gives the determination of phenol by the same method as used for determining the cresols. The method does not vary from Wilkie's, except that the concentrations of the reagents are so chosen that with continuous shaking for one minute the reaction is complete. This rapid reaction leaves the precipitate a flocculent, white or pinkish mass and does not obscure the iodine-starch color, requiring thereby no filtering off of the precipitate as in Wilkie's method, which allows ten minutes for the "reaction period" and as a consequence a filtering off of the dark red precipitate is required. In Experiment 26, the 25 minutes' shaking had made the precipitate so dark that the determination could not be made without filtering.

Experiments 19 and 20 show that *N*/10 sodium bicarbonate is not sufficient to complete the reaction in 1 minute. Fifteen minutes are required for its completion under these conditions (Expt. 21). Sodium bicarbonate *N*/4 was used in Expt. 22 and was found to be sufficient with one minute's reaction period. One minute is sufficient time to complete the reaction with *N*/2 bicarbonate and when 25 minutes was allowed for the reaction no further absorption of iodine took place. The precipitate was a lilac-pink. With less phenol and the same amount of iodine (Experiment 26); the precipitate was a dark wine color and obscured the end point in titrating back with thiosulphate for excess iodine. A precipitate appeared in Experiments 19 to 21, but no precipitates formed in Experiments 23 to 26 until the acid was added.

DETERMINATION OF A MIXTURE OF *o*-, *m*- AND *p*-CRESOL.

A solution was made up by taking one-third by weight of each of the cresols and diluting until the strength of the solution contained (108.064/60) grams cresols per liter. The results are given in Table V. In the second last column is given the amount of iodine absorbed by the cresols and the last column represents the amount of iodine which should have been absorbed, calculated for the amount of cresols in the solution (reckoning the ortho- and para-cresols as di-iodo-cresols and the meta-cresol as the tri-iodo-cresol). The error in each case is 0.2 per cent and reckoned as an error for any one of the three cresols represents a loss of 0.6 per cent, since they are each present in equal amounts, or if the error be distributed over each of the three ingredients, it is an error in each of 0.2 per cent.

TABLE V.—DETERMINATION OF MIXTURES OF *o*-, *m*- AND *p*-CRESOLS.

Ex. No.	$NaHCO_3$ Cc.	Water Cc.	Cresol mixtures Cc.	Iodine Cc.	Reaction period, Min.	2 *N* acid added Cc.	Thio Cc.	*N*/10 iodine absorbed Cc.	Calculated iodine absorption Cc.
27..	25	75	15	40	1	25	1.5	11.75	11.73
28..	25	75	15	40	1	25	1.5	11.75	11.73
29..	25	75	14	40	1	25	2.3	10.97	10.95

For solutions, etc., see Table VI.

A MIXTURE OF PHENOL, *o*-, *m*- AND *p*-CRESOL.

The equation of Ditz to determine the amounts of *m*-cresol in the presence of *o*- or *p*-cresol, and modified later by Siegfried and Zimmermann for determining phenol in the presence of *p*-cresol may be extended to include the determination of phenol, *o*-, *m*- and *p*-cresol in the presence of all four compounds and with these equations, if there be known (1) the weight of the mixture present; (2) the total amount of iodine absorbed; the following determinations may be made from a single titration:

(1) The meta-cresol present.
(2) The phenol present.
(3) The sum of the *o*- and *p*-cresols present.

If x = weight of (phenol + *m*-cresol),
y = weight of (*o*- and *p*-cresol),
m = total weight taken of the mixture,
c = effective formula weight of phenol and *m*-cresol.
a = weight of phenol present,
b = amount of *m*-cresol,
n = number of mols of iodine disappearing,

Then

$$x + y = m \qquad (1)$$

$$\frac{3x}{c} + \frac{2y}{108.064} = \frac{n}{2} \qquad (2)$$

$$a + b = x \qquad (3)$$

$$\frac{a}{94.048} + \frac{b}{108.064} = \frac{x}{e} \qquad (4)$$

$$\frac{108.064 - e}{e - 94.048} = \frac{108.064\ a}{94.048\ b} \qquad (5)$$

Of the above quantities, n is known and is the amount of iodine disappearing or absorbed.

m is known and is the amount of the mixture of cresols and phenol weighed out into the solution.

x, y, e, a, b are five unknowns, and with the five independent equations given, they may be obtained.

This method is limited since the amount of the mixture m is obtained by weighing, and no impurity can be present without affecting the results. Further, it can be seen from the nature of the equations containing e that small variations in the determination of e affect the value of a and b considerably. However, if the dried precipitate of the iodo compounds were weighed after the titration with the thiosulfate a different value for m would be obtained; m would then represent the weight of the halogenated mixture, not the mixture itself. Equation (1) will become

$$x + y + (127.96)\ N/2 - (1.008)\ N/2 = m.$$

The equation is useful for analyzing mixtures containing water and other compounds which do not halogenate and which prevent the weighing of the mixture before precipitation with the iodine. The determination by the iodine and sodium bicarbonate is as accurate as the operator chooses to make it. Using large volumes of solutions (50 cc.) and allowing at least 8 minutes for the solution to run out of the 50 cc. burettes, very accurate results can be obtained.

TABLE VI.—DETERMINATION OF MIXTURES OF PHENOL, ORTHO-, META- AND PARA-CRESOL.

Ex. No.	$NaHCO_3$ Cc.	Water Cc.	Cresol mixtures Cc.	Iodine Cc.	Reaction period, Min.	2 N acid added Cc.	Thio Cc.	Actual iodine absorption per Cc.	Calculated iodine absorption Cc.
30..	25	75	20	60.0	1	25	4.02	15.88	15.99
31..	25	75	20	60.0	1	25	3.83	16.08	15.99
32..	25	75	20	60.0	1	25	3.95	15.96	15.99

Thiosulfate = 0.0982 N. Sulfuric acid = 2 N. Temperature = 23° C. Iodine = 0.03306 N. Sodium bicarbonate = N.

Table VI gives the results of three successive titrations of a mixture composed of equal volumes of solutions of phenol, *o*-, *m*- and *p*-cresol having the following strengths:

Phenol = 0.09060 N
o-Cresol = 0.06800 N.
p-Cresol = 0.06800 N.
m-Cresol = 0.09850 N.

The second last column gives the amount of iodine absorbed by the mixture. The last column gives the amount which should have been absorbed calculated from the amount of materials added to the mixture. The error varies from 2 parts to 5 parts per thousand. If the discrepancy be calculated over the four ingredients the error is 0.2 to 0.5 per cent. If the error be calculated as due to one single substance present the determinations vary by 0.8 to 2.0 per cent, since the substances are present in equal amounts by weight.

DETERMINATION OF THYMOL.

The assumption is very general in the literature that time is an important factor in the halogenation of aromatic compounds. This is especially true for the more highly substituted phenolic bodies. Fifteen minutes to one hour is recommended as the time for complete halogenation. The assumption that this rate of reaction is comparatively slow seemed untenable. If complete diffusion be effected by continuous shaking the reaction should be complete in a very short time. To test this, the determination of thymol (3-methyl-6-isopropyl phenol) was undertaken.

The iodine-sodium bicarbonate method was applied to the determination of thymol and the results are given in Table VII. The calculations are made for the thymol strength, assuming that two iodines enter the ring giving di-iodo-thymol.

TABLE VII.—DETERMINATION OF THYMOL.

Ex. No.	H_2O Cc.	$NaHCO_3$ Cc.	Thymol Cc.	Iodine Cc.	Reaction period, Min.	H_2SO_4 Cc.	20 per cent KI Cc.	Thiosulfate Cc.	Per cent of thymol found.
33.....	100	25	15	27.4	2	25	..	1.72	100.0
34.....	100	25	10	18.0	1	25	..	1.07	100.0
35.....	100	25	5	32.25	1	25	..	7.79	122.6
36.....	100	25	15	32.0	1	25	..	3.20	100.8
								3.30(*a*)	99.6
37.....	100	25	15	30.0	1	25	5	2.58	100.2

Iodine = 0.03306 N. Sulfuric acid = 2 N. Thio = 0.0982 N. Sodium bicarbonate = N. Thymol = 0.0491 N. Temperature = 23° C.

(*a*) This result was obtained by titrating the blue color, which returned after the first titration. The time allowed for the blue to return was 10 minutes. The blue did not return in one-half hour after the second titration.

Experiments 33 and 34 show that the iodination is complete in one minute. Seidell[28] states that one-half hour must be allowed for thymol to be brominated. This is true only in case the diffusion is incomplete. If the free iodine is in excess (300 per cent), as in Experiment 35, the hydroxyl is partly filled with iodine and gives a determination 22 per cent too high, calculated as the di-iodo-thymol. Experiment 36 indicates that the iodine which is absorbed in the hydroxyl will be freed in a few minutes if the precipitate is left in contact with the small amount of hydriodic acid, which has been formed in the solution. The reduction can be seen in the rapid return of the blue color. This return of the blue continues only until the iodine in the hydroxyl has been completely liberated. An addition of 5 cc. of 20 per cent KI reduced the di-iodo-thymol bromide in one minute to the di-iodo-thymol

[28] Am. Chem. J., 47, 519 (1912).

and the blue color does not return rapidly (*i. e.*, within one hour).

In working with the cresols and phenol the blue did not return except in the case of the ortho-cresol. The reading was taken after the blue ceased to return (5 to 10 minutes). No KI was added. However, it is advisable to use KI if the experiments show a tendency for the blue color to return within five or ten minutes. The free hydriodic acid produced in the acid solution by this addition reduces[29] the thymol iodide completely, with one minute's shaking. Wilkie states that his determinations were all high (1½ per cent). The explanation lies probably in the fact that the iodine is partly absorbed into the hydroxyl and as the iodo precipitate is filtered off in his method, there is no possibility of its reduction.

DIRECTIONS FOR DETERMINING PHENOLIC COMPOUNDS.

First. Solutions required: 0.1 *N* sodium thiosulfate, 24.8 grams per liter; 0.03 *N* iodine solution, 12.7 grams per liter; *N* sodium bicarbonate; 2 *N* sulfuric acid; 0.5 per cent starch solution.

Second. Into a 500 cc. ground stoppered bottle, put 50 cc. water and 50 cc. of approximate *N* sodium bicarbonate, add 15 cc. of the unknown solution of the phenolic compound which has been previously diluted to approximately 0.1 *N*.

Run in the iodine solution until the mixture in the bottle remains a permanent brown iodine color; 20 per cent excess is recommended. Stopper the bottle firmly and shake it well for one minute.

Third. Add carefully, at first, to prevent excessive bubbling, 50 cc. of 2 *N* sulfuric acid. Shake well and titrate the excess iodine with the thiosulfate, using starch as indicator. Occasionally blue color returns rapidly after the end point has been first reached. For such determinations it is best to add 5 cc. of 20 per cent KI to hasten the freeing of the iodine which is held in the hydroxyl. The final end point after the blue ceases to return is the correct reading for the thiosulfate. All the solutions should be at 20° to 25° C.

SUMMARY.

I. Rapid and accurate determinations of *o*-, *m*-, and *p*-cresol, phenol and thymol have been effected by the use of iodine solutions in the presence of sodium bicarbonate.

II. The method is equally rapid and accurate for all five compounds, the error for each compound being within 0.2 per cent.

III. The "reaction period" for these determinations is one minute, when the shaking is continuous.

IV. The sum of the cresols present in a mixture may be determined within a total error of 0.2 per cent.; the *m*-cresol may be determined in the presence of *o*- and *p*-cresol by this method.

V. A series of simple equations are given which will permit the determination of phenol, meta-cresol and the sum of the ortho- and para-cresols in the presence of each other in any combination or proportion if two quantities be known.

(*a*) The weight of the mixtures taken.

(*b*) The amount of iodine absorbed.

VI. Results of experiments are given which show that these four compounds can be determined in the presence of each other by this method within an error of 0.2 to 0.62 per cent, calculated on the sum of the materials present.

[29] Werner Jahresber., 633 (1866). Lloyd, J. Am. Chem. Soc., 27, 16 (1905).

PROPOSED METHOD FOR DETECTING ADULTERATION OF CIDER VINEGAR WITH DISTILLED VINEGAR.*

By S. L. CRAWFORD.

At the present time it is only possible to determine whether a cider vinegar has been adulterated with an appreciable amount of distilled vinegar, providing the different constituents have not been raised to cover up the addition of the distilled vinegar. The glycerine determination, for example, is only valuable providing a sufficient amount of glycerine has not been added to the vinegar to make up for the lowering of the glycerine content caused by the addition of distilled vinegar. Therefore, in looking for a way of determining whether cider vinegar contains added distilled vinegar, our principal aim has been to find some difference between cider vinegar and distilled vinegar, which could not be affected by additions made to the vinegar.

It has been known for some time that there was in cider vinegar a volatile constituent which had a reducing effect on Fehling's solution, and in order to get the true amount of reducing sugars in vinegar, it is necessary to evaporate several times after the addition of water. What this substance is, has not yet been determined, but what we found was that while distilled vinegar or pyroligneous acid does not contain any appreciable amount of this volatile substance, all cider vinegar shows its presence in sufficient amount to make it a valuable constant in determining the purity of a vinegar.

The proposed method is to take 50 cc. of sample, dilute to 250 cc. and distil over 200 cc. into a 250 cc. flask. Neutralize and make up to the mark. Take 50 cc. of this distillate and determine sugars by the method given in Bureau of Chemistry, Bulletin 107. The result is given as invert sugar according to Munson and Walker's tables.

In Table I are shown results determined on seven different samples of distilled vinegar obtained from different sources, and of varying age running from one month to one year. It will be seen from the figures given in Table I that distilled vinegar when reduced to 4 per cent acid strength contains from a trace to 0.0026 gram per 100 cc. of this volatile substance, which is practically negligible.

In Table II is given the amount found in a fully

*From the Journal of Industrial and Engineering Chemistry.

fermented dry refined cider six months old, and a completely fermented first pressing juice, which has not been refined, also six months old. As only traces were found in these samples, it goes to show that the volatile substance is produced during the acetification of the apple juice.

Table III shows the amount found in four samples of cider vinegar made from first pressings, having an average of 0.162 gram on a 4 per cent basis.

TABLE I.

Sample	Composition	Acid Grams 100 cc.	Vol. red. substance Grams 100 cc.	Red. to 4 per cent basis
1	Distilled vinegar....	10.0	0.0065	0.0026
2	Distilled vinegar....	9.44	Trace	Trace
3	Distilled vinegar....	10.67	Trace	Trace
4	Distilled vinegar....	9.01	0.0005	0.0002
5	Distilled vinegar....	10.46	0.0045	0.0017
6	Distilled vinegar....	9.61	0.0010	0.0004
7	Distilled vinegar....	10.38	Trace	Trace

TABLE II.

Sample	Composition	Acid Grams 100 cc.	Vol. red. substance Grams 100 cc.
8	Dry refined cider.....	0.36	Trace
9	1st pressing	0.75	Trace

TABLE III.

Sample	Composition	Acid Grams 100 cc.	Vol. red. substance Grams 100 cc.	Red. to 4 per cent acid basis
10	1st press	4.70	0.2232	0.190
11	1st press	4.70	0.2051	0.174
12	1st press	4.50	0.1664	0.148
13	1st press	4.20	0.1424	0.136

TABLE IV.

Sample	Composition	Acid Grams 100 cc.	Vol. red. substance Grams 100 cc.	Red. to 4 per cent acid basis
14	2nd press	5.53	0.2244	0.162
15	2nd press	4.62	0.2092	0.181
16	2nd press	4.20	0.1784	0.170

TABLE V.

Sample	Percentage composition 1st press	2d press	Acid Grams 100 cc	Vol. red. substance Grams 100 cc.	Red. to 4 per cent acid basis
17.....	75	25	4.98	0.1824	0.147
18.....	66.7	33.3	4.48	0.1405	0.125
19.....	75	25	4.72	0.1752	0.149
20.....	75	25	4.86	0.1621	0.133
21.....	85	15	4.96	0.1384	0.111
22.....	66.7	33.3	4.72	0.1562	0.133
23.....	75	25	4.82	0.1520	0.126
24.....	50	50	5.52	0.1700	0.123
25.....	50	50	5.69	0.1840	0.129

In Table IV are the amounts found in three samples of cider vinegar made from second pressings, all kept different lengths of time before repressing. Sample No. 14 was repressed the second time one hour after the first pressing; No. 15 nineteen hours after the first pressing; and No. 16 was repressed five days after the first pressing.

As these figures are fairly constant, it does not appear to make any appreciable difference in the amount of volatile reducing substance present, how long the pomace is kept before repressing.

Table V shows nine samples of cider vinegar composed of varying amounts of first and second pressings, and it will be seen that the amount of volatile substance found is fairly constant when reduced to a 4 per cent basis, running from 0.111 to 0.149.

All of the above samples are of known purity and all comparatively new vinegars, none of them being more than one year old.

While the above figures are not sufficient evidence upon which to determine the purity of a cider vinegar, it would seem from the work done, that if a large number of vinegars of varying composition and age were examined, a maximum or minimum content for cider vinegar could be found, which would, in addition to the known glycerine content and other constants, be of considerable aid in determining whether a cider vinegar has been adulterated with distilled vinegar or pyroligneous acid.

If desired, it can be readily determined whether the adulteration is due to the presence of distilled vinegar or pyroligneous acid, owing to the fact that if pyroligneous acid has been used, the vinegar will contain more than 0.007 gram per 100 cc. of formic acid, while if distilled vinegar has been used, the amount of formic acid present will be below 0.007 gram per 100 cc., depending upon the amount of cider vinegar present in the mixture. A pure cider vinegar when subjected to the formic acid test will show from a trace to 0.007 gram per 100 cc. of a substance which is calculated in this determination as formic acid.

We give below the analysis of a vinegar actually made from distillery slop and distilled vinegar. It will be seen that if this vinegar was branded "reduced with water" to take care of the low non-sugars and ash, it would be impossible for any chemist to prove that it was not a pure cider vinegar.

Specific gravity at 20° C.	1.0145
Acetic acid, grams per 100 cc.	4.86
Solids, grams per 100 cc.	1.97
Reducing sugars before inversion, grams per 100 cc.	0.70
Ash, grams per 100 cc.	0.209
Alkalinity of ash, cc. N/10 acid.	29.60
Phosphoric acid soluble, mgms. per 100 cc.	6.98
Phosphoric acid insoluble, mgms. per 100 cc.	17.38
Polarization degrees Ventzke	—1.6
Formic acid, grams per 100 cc.	Absent
Glycerine, grams per 100 cc.	0.292
Volatile reducing substance, grams per 100 cc.	Absent
Lead precipitate	Good
Artificial color	None detected
Non-sugars, grams per 100 cc.	1.27
Per cent of solids reducing sugars	35.50
Ratio of ash to non-sugars.	1.6

One form of adulteration which the above method would be useful in detecting is when the slop or residue from an apple brandy still is mixed with a weak solution of alcohol and run over the generators, or distilled vinegar is added direct, artificially colored and sold as cider vinegar.

As practically every constituent of the apple is left unchanged in the still after distillation, it is almost impossible to detect this form of adulteration by any of the regular methods of analysis, for nothing has been taken away from the original apple juice except the alcohol, and that is replaced either with other alcohol or its equivalent of acetic acid. A vinegar of this kind, however, contains either no volatile reducing substance or only a trace, due to the small amount present in the distilled vinegar, as the original apple juice has never undergone the acetic fermentation, at which stage the volatile reducing substance is formed. For this reason the adulteration can be readily detected.

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NOTES AND COMMENTS.

Search for Potash Deposits.

Field work undertaken by the United States Geological Survey in the search of potash has heretofore been largely of an exploratory character, according to the annual report of the Director recently made to Secretary Lane, but during the last year important principles have been established which will be of material assistance in future work. During the year a number of shallow drill holes were sunk in some of the prehistoric lake basins in Nevada and California, and a careful study was made of some of these lakes. Some of these experiments are yielding significant and perhaps important results. When areas that may prove to be of value as sources of potash are discovered, the public land included in such areas is withdrawn from entry until its value for potash can be demonstrated or disproved. As a result of the Survey's reconnaissance examinations in California and Nevada, 133,829 acres have been included in potash withdrawals.

Baking Powder in the Netherlands.

The U. S. Consul at Amsterdam reports that no American baking powder is on sale in that city. Nothwould consider very inferior substitutes. A reason given therefor is that few families do any baking, but buy their bread and cakes from professional bakers. Another possible reason may be the relatively high duty in this country on imported articles hermetically sealed, which include canned baking powder. While the general rate of duty is 5 per cent ad valorem, the duty on canned and bottled goods is specific and amounts to about 4½c a pound. Thus, if the duty were added to selling price, a pound can of baking powder costing about 45 cents in England, where great quantities of American baking powder are used, would cost about 50 cents here.

But this difference of 5 cents would not seem to be an insuperable obstacle to the sale of canned baking powder in Holland, because American fruits and vegetables in hermetically sealed containers are found in all the large provision stores in Amsterdam. The prices are higher than in the United States and England, but nevertheless there is a sufficient steady demand for the articles to warrant their being kept in stock. This tends to show that the duty does not prevent the sale of baking powder here. The probably true explanation is that the people are not acquainted with it, and that to create a demand they must be given to understand through some form of practical demonstrations what advantage there is in using baking powder. It is worth the consideration of American manufacturers of baking powder whether such demonstrations, to which the public would be invited, could not be given with profitable results in Amsterdam and other Dutch cities.

The Approximate Melting Point of Some Commercial Copper Alloys.

As very little information on the melting points of commercial brasses and bronzes can be found in either scientific or technical literature, tests of a few typical alloys were made by H. W. Gillett and A. B. Norton of the U. S. Bureau of Mines. The results, summarized, in Technical Paper No. 60, are as follows:

Alloy.	Approximate Composition. Copper.	Zinc.	Tin.	Lead.	Melting Point. °Cent.	°Fahr.
Gun metal	88	2	10	..	995	1825
Leaded gun metal	85½	2	9½	3	980	1795
Red brass	85	5	5	5	970	1780
Low-grade red brass	82	10	3	5	980	1795
Leaded bronze	80	..	10	10	945	1735
Bronze with zinc	85	5	10	..	980	1795
Half-yellow-half-red	75	20	2	3	920	1690
Cast yellow brass	67	31	..	2	895	1645
Naval brass	61½	37	1½	..	855	1570
Manganese bronze	..	..	..	..	870	1600

The melting point given is the "liquidus," or point where the alloy is completely molten. The temperatures are thought to be accurate within plus or minus 10° C. or plus or minus 20° F.

Estimates for U. S. Bureau of Mines for 1914-15.

The estimates of appropriations for the United States Bureau of Mines, for the fiscal year ending June 30, 1915, as approved by Secretary Lane of the

ing of that nature is found except what Americans Interior Department, have just been forwarded to Congress.

The estimates are as follows: For general expenses of the Bureau of Mines, $70,000; for investigating mine accidents, $347,000; for the equipment of mine rescue cars and stations, $30,000; equipment of testing plant at Pittsburgh, Pa., $10,000; for testing fuels, $135,000; for mineral mining investigations, $120,000; for inquiries and investigations of petroleum and natural gas, $30,000; for inspection of mines in Alaska, $7,000; for books and publications, $2,000; for lands, leases, etc., for mine rescue cars, $1,000. The total for the Bureau of Mines is $752,000, an increase over the fiscal year ending June 30, 1914 of $90,000. The item of $30,000 for the equipment of rescue cars and stations is for the first time placed separately in the estimates and represents an increase. The $10,000 asked for the equipment of the testing plant is a new item. The money is needed for the purchase of steam and electric equipment. The estimates set forth that the present power and electric service plant at the experiment station is on the eve of breakdown.

For the mineral mining investigations, an increase of $20,000 is asked, from $100,000 to $120,000.

For the inspection of mines in Alaska, an increase of $500 over the previous year is asked. The same increase is asked for books and publications. The item for lands, leases, etc., for mine rescue cars is decreased $1,000.

The item of $30,000 for inquiries and investigations of petroleum and natural gas is for the first time placed separately in the estimates and represents an increase. It calls for inquiries and investigations concerning the mining, preparation, treatment and utilization of petroleum and natural gas, with a view to economic development, and conserving resources through the prevention of waste. On this subject, the estimates contain the following statement:

In 1911 the total value of the petroleum produced in this country was $134,044,752; that of the natural gas usefully produced was $74,127,534. The magnitude of the petroleum industry, the increasing value of petroleum and natural gas as fuel, and the rapid decline of the yield from many fields emphazise the need of conducting inquiries concerning the mining, treatment and utilization of petroleum and natural gas, with a view to economical and efficient development of these resources, as well as inquiries into the economic conditions that have developed in the oil and gas industries, with a view to the determination of the factors governing production and the means whereby supplies of oil and gas, especially those on public lands or on lands controlled by the government, can be utilized to best advantage in promoting the public welfare.

As illustrating the need for inquiries and investigations concerning petroleum and natural gas, with a view to economic development, it is pertinent to note the following extract from a recent report received by the Bureau of Mines regarding the Cushing field of Oklahoma: "The maximum yield of oil from the Cushing field has never reached 30,000 barrels per day. For a long period it has been considerably less than 20,000 barrels per day. The average value of oil at the highest market quotation probably lies below $20,000 per day. During this time there has been wasting from drilling wells not less than 100,000,000 cubic feet of gas.

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